



The role of CO₂ flushing in triggering the 'Millennium' eruption and recent unrests at Changbaishan volcano (China/North Korea)

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Keywords:	Plumbing system modeling, CO ₂ flushing, Slab dehydration, Triggering mechanism, Storage depth, Changbaishan volcano

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3 | 1 **The role of ~~stagnant slab-derived fluids~~ CO2 flushing in triggering the ‘Millennium’ eruption**
4 | 2 **and recent unrests at Changbaishan volcano (China/North Korea)**
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Abstract The impact of large-scale caldera-forming eruptions on our society and climate can be considerable. The triggering mechanisms of these eruptions and the instability of their magmatic systems are still elusive. Here we use X-ray tomographic microscopy, glass geochemistry and volatile element concentration data on the products of the 946 CE ‘Millennium’ eruption (ME) of Changbaishan volcano (China/North Korea) with the aim to identify the triggering mechanism of the eruption. ME emitted rhyolites and trachytes whose textural parameters suggest vesiculation events related to crystallization and magma ascent in the conduit, and to the arrival of new gas in the magmatic system. Solubility models show that the CO₂ and H₂O dissolved in the glass are consistent with a pressure of 100-200 MPa. Literature data from fluid inclusions in minerals indicate that the residing magma was CO₂ free before the eruption, whereas the CO₂ content in the glass reaches 600 ppm at the flash of the ME event. We find that a single, shallow magma reservoir localized between 7.5 and 3.7 km depth in which rhyolites occupies the top and trachytes the bottom is fully destabilized by the arrival of external CO₂-rich fluids. Such fluids are released from a deeper, metasomatized carbonate-rich mantle source ~~enriched associated to the dehydration of the 500 km deep stagnant Pacific slab.~~ Our results and those of independent geophysical data show that the ME magmatic system is still active, and the continuous upraising of fluids from depth may drive unrest episodes like that recorded in 2002-2006. Our findings elucidate the role of larger scale geodynamic processes as the ascent of slab-derived deep deep, mantle-derived fluids in driving large-scale explosive eruptions. We provide evidence that volcanic unrests may not mirror the internal dynamics of magmatic reservoirs.

Keywords: Changbaishan volcano; Plumbing system modeling; Triggering mechanism; CO₂ flushing; Slab dehydration; Storage depth

1. Introduction

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3 58 Large-scale caldera-forming eruptions emit hundreds of km³ of magma and are among the most
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5 59 catastrophic natural events on Earth. Their effects on our society may be dramatic (Robock, 2000;
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7 60 Bryan, *et al.*, 2010); Brown *et al.*, 2014; Papale and Marzocchi, 2019). In the last 10000 years, 17
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9 61 eruptions with magnitude $M \geq 7$ have been recognized with at least 2 events occurred in the last 1000
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11 62 years (Croweller *et al.*, 2012; Oppenheimer *et al.*, 2017; Newhall *et al.*, 2018): the 1815 CE, $M = 7$
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13 63 eruption at Tambora, Indonesia, and the 946 CE, $M = 7.4$ ($M = 6.4 \div 7.2$ following Yang *et al.*, 2021)
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15 64 ‘Millennium’ eruption at Changbaishan volcano, China/North Korea. The knowledge of the geometry
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17 65 of the magmatic system associated to eruptions of a such size and of their triggering mechanisms is
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19 66 crucial to appropriately understand the monitoring signals during unrest episodes and assess the
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21 67 volcanic hazard (Acocella *et al.*, 2015). However, two still debated questions on large-scale eruptions
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23 68 concern (a) the occurrence of a huge, single magma chamber or of different reservoirs at different
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25 69 depth (Jellinek *et al.*, 2003; Cashman and Giordano, 2014; Kruger and Latypov, 2020). and (b) the
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27 70 mechanisms leading to eruption. Magma mixing, buoyancy (Caricchi *et al.*, 2014; Malfait *et al.*, 2014;
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29 71 Bergantz *et al.*, 2015), variations in volatile and crystal cargo content (Wark *et al.*, 2007), far-field
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31 72 tectonic stress (Costa *et al.*, 2016; Cabaniss *et al.*, 2018), and gas injection with dislocation and/or
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33 73 melting of the crystal-mush (Bachmann and Bergantz, 2006; Parmigiani *et al.*, 2014) have been
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35 74 proposed as leading mechanisms. The above summarized issues point out that our comprehension of
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37 75 large-scale magmatic systems is limited. Here we present X-ray tomographic microscopy textural and
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39 76 geochemical (glass composition and dissolved H₂O, CO₂, S, F and Cl) data on the pumices and scoriae
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41 77 of the ~~largest eruption of the last millennium, the M=7.4~~ 946 CE ‘Millennium’ eruption (hereafter
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43 78 ME) at Changbaishan, an intraplate volcano at the China/North Korea border characterized by a 5 km
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45 79 wide summit caldera (Fig. 1A). We reconstruct the magma storage conditions and degassing
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47 80 processes of ME, calculate the depth of the reservoir, and recognize the roof rupture mechanism. We
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49 81 show that the ME magmatic system is still active and periodically shaken by the injection of
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51 82 ~~slabmantle~~-derived fluids. We explain the signals of the 2002-2006 unrest episode at Changbaishan
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53 83 as due to the upraising of ~~these~~ fluids ~~from the mantle~~ and focus on ~~the~~~~their~~ role ~~of such deep fluids~~

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3 84 in the triggering mechanism of large-scale caldera forming eruptions. Our results provide a new
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5 85 perspective on the instability mechanisms of large magmatic systems, their link with larger scale
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7 86 geodynamic processes, i.e. deep degassing, with obvious implications for the volcano monitoring
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9 87 strategies and volcanic hazard assessment at calderas.
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12 88

15 89 2. Geodynamic and volcanological setting and the 946 CE ‘Millennium’ eruption

17 90 Changbaishan volcano is located west of the Japan trench above the 500 km deep stagnant slab
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19 91 of the Pacific subduction (Fig. 1B; Lei *et al.*, 2013; Zhang *et al.*, 2018). Lei *et al.* (2013) detect a low
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21 92 velocity zone at 400 km depth possibly reflecting the fluid release and dehydration of the subducted
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23 93 Pacific slab. Changbaishan started its activity ~5 Ma ago with eruptions fed by basaltic, and later
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25 94 trachytic, magmas; in the last 0.04 Ma, pre-caldera silicic lava flows and caldera-forming eruptions
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27 95 occurred including ME (Zhang *et al.*, 2018; Pan *et al.*, 2020). Minor eruptions are postulated in 1403
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29 96 CE, 16881668 CE and 1702 CE (Sun *et al.*, 2017). However, Pan *et al.* (2017) report that the deposits
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31 97 attributed to these historical events represent the final phase of the ME. Changbaishan volcano
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33 98 suffered an unrest episode between 2002 and 2006 with changes in gas geochemistry, ground uplift
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35 99 and increase in the seismic rate (Xu *et al.*, 2012). CO₂-rich degassing areas and hot water emissions
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37 100 are widespread on Changbaishan with CO₂ discharge values up to 9.4×10^5 t/yr (Zhao *et al.*, 2021).
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39 101 According to the available geochemical data, such fluids are released from recycled carbonates and
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41 102 organic metasediments ~~ofmetasomatizing~~ the ~~Pacific stagnant slab and metasomatize overlying~~
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43 103 mantle (Fig. 1B; Zhang *et al.*, 2015; Hahn *et al.*, 2008; Wei *et al.*, 2016; Xu *et al.*, 2020). A
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45 104 widespread release of CO₂ of mantle origin ($\delta^{13}\text{C} = -5.5 \pm 2.5\%$; He with R/Ra between 3.21 and 4.96)
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47 105 also characterizes other, large non-volcanic areas in NE China, e.g. the Songliao basin located 200
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49 106 km north of Changbaishan (Liu *et al.*, 2018). Here, 146 wells distributed over an area of about 33700
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51 107 km² contain a CO₂ percentage between 6 and 99%, testifying the regional scale accumulation and
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53 108 degassing of CO₂ from the stagnant slab mantle in NE China (Zhang *et al.*, 2018; 2020).
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ME of Changbaishan emitted $96 \pm 19 \text{ km}^3$ (Dense Rock Equivalent, DRE = $24 \pm 5 \text{ km}^3$) of pyroclastics (Horn and Schmincke, 2000). [Yang et al. \(2021\)](#) report a volume of $40\text{--}98 \text{ km}^3$, VEI = 6 and $M = 6.4 \div 7.2$. The column height was estimated $>25 \text{ km}$ and the fall deposits show an eastward dispersion with ashes found in Japan Sea, Japan mainland, Eastern Russia, and Greenland (Sun et al., 2014; McLean et al., 2016). ME deposits consist of an extensive white, nearly aphyric, rhyolitic pumice fallout and ignimbrite (95 vol.% of tephra), overlain by a fallout of dark, phenocryst-rich (30% vol.% of crystals), trachytic scoriae distributed on the crater rim and northeastern flank of Changbaishan ([Machida et al., 1990](#); Pan et al., 2017, 2020; Yi et al., 2021) (Fig. 1, C and D). Subordinates mingled rhyolite-trachyte clasts are interpreted as the result of the syn-eruptive interaction between the two magmas in the conduit (Pan et al., 2017; Yi et al., 2021). Although the rhyolite results from the fractionation of the trachytic magma, the geometry of the magmatic system is debated. Two models have been proposed: a large, single magma chamber (Iacovino et al., 2016) or two separated sill-like reservoirs occupied by different but consanguineous trachytic and rhyolitic magmas (Horn and Schmincke, 2000).

3. Analytical methods

3.1 Rock samples

The examined ME rocks are rhyolitic pumices and trachytic scoriae, collected from proximal and distal outcrops of basal fallout and ignimbrite as well as upper fallout deposit, respectively. Sampling sites are summarized in Fig. 1C. Particularly, representative samples were selected based on the collected juvenile component by Yi et al. (2021) as these authors systematically analyzed the petrography, whole-rock chemistry, Sr-Nd isotopes, and minerals of pumices and scoriae, thus. Thus these data constitute a robust background for our new textural and chemical analyses.

Particularly, most of the samples (9 samples: three from ~~white~~yellow pumice fallout, three from ~~black~~dark scoria fallout and three from gray/~~green~~ pumices fallout) come from the proximal outcrops where the stratigraphic relationship between the different eruptive units is well preserved (Yi et al.,

2021); ~~however for comparison also~~. However, two samples from distal fallout and one from ignimbrite deposits were also selected for comparison. Pumice and scoria samples are analysed by Electron Micro Probe Analyzer (EMPA) for major elements, Cl and F concentrations in matrix-glasses; H₂O as well as CO₂ and S contents are measured on matrix-glasses fragments by thermogravimetric (TGA) and Carbon/Sulfur Analyses (CSA), respectively. Samples are also inspected through Scanning Electron Microscope (SEM) and microtomographic analysis. Details on the samples and the results of the above summarized analyses are reported in the Supplementary data.

3.2 EMPA and SEM analyses

EMPA analyses have been performed at the HP-HT Laboratory of Experimental Volcanology and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome (Italy), using a Jeol-JXA8200 Electron Micro Probe Analyzer equipped with five wavelength dispersive spectrometers. Samples were analyzed under high vacuum conditions, using an accelerating voltage of 15 kV. The electron beam current was set at 7.5nA. Elemental counting times were 10 s on the peak and 5 s on background positions. Corrections for inter-elemental effects were made using a ZAF (Z: atomic number; A: absorption; F: fluorescence) routine. For each analysis, a defocused beam was used to minimize losses of alkalis and volatiles, which were counted first to avoid diffusion effects. The following standards have been adopted for the various chemical elements: jadeite (Si and Na), corundum (Al), forsterite (Mg), andradite (Fe), rutile (Ti), orthoclase (K), barite (Ba), Celestine (S), fluorite (F), apatite (P and Cl), and spessartine (Mn). Data reduction was carried out using ZAF4/FLS software by Link Analytical. Accuracy was better than 1–5% except for elements with abundances below 1 wt.%, for which accuracy was better than 5–10%. Samples were also inspected through backscattered electron (BSE) 2D images collected using a SEM JEOL JSM-6500F and operating at 15 kV at INGV in Rome.

3.3 Thermogravimetric (TGA) and Carbon/Sulfur (CSA) analyses

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3 161 The collected juvenile samples, in particular the pumices, were carefully treated and examined.
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5 162 First of all, they were stored overnight in a bath of H₂O₂ (aqueous solution at 20%) to ~~avoid the~~
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7 ~~presence of~~remove organic materials. After this treatment, the samples were left in air to dry for 24 h
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10 164 and ~~successively~~ stored overnight in a drying box at 35-40°C, to release also the water possibly
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12 165 absorbed from the glass surface. The samples were then cut by a low-speed diamond saw and the
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14 inner pattern of bubbles of each sample was examined to select the samples more suitable for
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16 analyses. The bubble size pattern exposed on the cut area helps in tracing the history of the nucleation
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18 event(s) that occurred before and during magma cooling. A pumice showing bigger vesicles in the
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20 center and smaller ones toward its rim surface was not considered for further investigations because
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22 such bubble pattern indicates that the vesiculation process continued after magma fragmentation
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24 170 during the pumice cooling. Only the pumices showing a homogeneous distribution of vesicles were
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26 171 further considered for the analyses. The juvenile samples were cut in a way to preserve only their
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28 172 core. In the case of samples containing phenocrysts (up to 2 mm), these were manually removed
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30 before measurements.
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35 175 Since the samples were too vesiculated and fragile to prepare as doubly polished thin
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37 ~~section~~sections for Fourier Transform Infrared Spectroscopy (FTIR) measurements, direct methods
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39 as TGA and CSA analyses were chosen to analyse the volatile contents of the matrix-glass samples.
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41 The measurements were performed at the Institute of Mineralogy of the University of Göttingen.
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43 Water contents ~~was~~were determined by TGA by using a Setaram TM TGA92. following the standard
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45 procedure described in Schmidt and Behrens (2008) and Behrens *et al.* (2009), about 20 mg of sample
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47 per measurement were filled into a Pt crucible and suspended to a balance in a graphite tube furnace.
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49 181 During a typical measurement, the sample is heated to 1200°C at a rate of 10°C/min in He flow and
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51 cooled at a rate of 30°C/min after a 30 min dwell time, ~~while the~~. The mass of the (dehydrating)
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53 sample is continuously recorded. ~~Since the~~The buoyancy of the suspended crucible and sample may
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55 change, for instance, with changing temperature, ~~once~~. Once a day, a blank measurement was
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57 recorded, consisting ~~in~~of an additional heating and cooling cycle performed on an already measured
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3 187 and consequently degassed sample. Blank measurements were subtracted from the sample signal in
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5 188 order to eliminate the effect of buoyancy on crucible and sample. For each sample, three-to-six
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7 189 thermogravimetric analyses were performed. The determination of the CO₂ and S content on matrix-
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10 190 glass samples was performed with an Elementar TM Inductar CS Cube, following the procedure
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12 191 described by Behrens *et al.* (2009). During a typical measurement, 0.5g Fe and 2g W are inserted
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15 192 together with 35 to 50 mg of crushed sample material into a ceramic crucible. The mixture is burned
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17 193 in an induction furnace at roughly 2000°C in an oxygen stream and the released CO₂ is measured by
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19 194 an Infrared (IR) cell. A typical day of analyses starts with a series of blank measurements without
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22 195 sample (0.5g Fe + 2g W only) followed by a series of measurements of steel standards with known
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24 196 CO₂ and S contents. The blank and the standard measurements are needed to daily calibrate the CSA
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26 197 and correct the analyzed experimental samples accordingly. TGA and CSA results show water and S
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28 198 contents lower or in the range of the values measured on not degassed melt inclusions, except for CO₂
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31 199 that is absent in melt inclusions measured by (Iacovino *et al.*, 2016).
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35 201 3.4 Microtomographic analysis

37 202 Microtomographic analyses have been performed using a Carl Zeiss Xradia Versa-410 3D X-
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40 203 ray microscope at INGV-Osservatorio Vesuviano in Napoli (Italy). Samples of diameter 1.5-3 cm
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42 204 were scanned in absorption mode, acquiring 4001 projections over a 360° rotation at 90-80 KV and
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44 205 8-7 W with objective 4x. The resulting nominal voxel (volumetric pixel) size is 4.48 µm. The
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46 206 tomographic reconstruction was achieved through a filtered back-projection algorithm using XRM
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49 207 Reconstructor software, thus producing a stack of 967 cross-sectional, grey-scale digital images.
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51 208 Image analyses were performed by using the Avizo (FEI) program and following the procedure
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54 209 described by Liedl *et al.* (2019).
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58 211 4. Results

4.1 Petrology and geochemistry of ME rocks

The glass-matrix compositions range from trachyte to rhyolite (comendite) (Fig. 2A). A clear compositional gap of about 5-10 wt% SiO₂ separates these two endmembers. Yi *et al.* (2021) find minor but ubiquitous mingled/mixed clasts in the ME products with SiO₂ ranging from 70 to 75 wt% on the basis of whole-rock analysis. These values only partially fill the compositional gap of observed SiO₂ in the glasses.

The rhyolitic pumices are phenocryst-poor (crystal content: ~0–10 vol.%, ~~constituted by~~ K-feldspar > clinopyroxene > olivine > quartz > Fe-Ti oxides > apatite), and show a glassy, vesicle-rich matrix (bulk porosity % between 71 and 73). By contrast, the trachytic scoriae are moderately vesiculated and porphyritic, with up to 30 vol.% crystals (K-feldspar > ~~pyroxene~~ clinopyroxene > olivine > Fe-Ti oxide > quartz > apatite) scattered in a dark microlite-bearing matrix-glass with porosity of 64% (see figures in the Supplementary data). Multi-banded clasts are also present and composed of dark, less vesicular and white vesicular bands; the porosity is between 68 to 73%. EMPA analyses indicate that the different bands in a single clast have homogenous trachytic or rhyolitic composition. K-feldspar phenocrysts show similar compositions in trachyte and rhyolite (Li *et al.* 2008). According to Yi *et al.* (2021), ~~pyroxene~~ Clinopyroxene phenocrysts are characterized by a decrease in Mg and Ca contents from trachyte to rhyolite; microlites have higher Ca content than phenocrysts, especially marked in trachytes (Fig. 2B).

Water, CO₂ and Cl are enriched in the sub-aphyric rhyolitic matrix-glasses (from 1.07 to 4.38 wt%, from 73 to 618 ppm and > 0.35 wt%, respectively) with respect to the trachytes (from 0.15 to 1.42 wt%, from 58 to 438 ppm and < 0.2 wt%, respectively); F and S abundances are more scattered in both compositions (rhyolite: F from 0 to 0.25 wt% and S from 12 to 165 ppm; trachyte: F from 0 to 0.25 wt% and S from 14, despite a datum at 1.6 ppm, to 195 ppm) (Fig. 3).

4.2 Microstructure

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3 237 The three-dimensional (3D) rock microstructure is investigated by X-ray microtomography on
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5 238 representative ME samples. Details and results are provided in the Materials and Methods section and
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8 239 in the Supplementary data. Based on their textural features, the analyzed samples can be separated
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10 240 ~~in~~ into three groups as follows:

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12 241 a) white pumiceous clasts (rhyolite) with a mean density value of 700 kg/m^3 containing rounded
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14 242 vesicles, although minor bands of elongated vesicles can be present. These clasts display Vesicle
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17 243 Number Density values (*VND*, the number of vesicles in each size class per unit melt or bulk volume)
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19 244 in the order of $3 \times 10^{11} \text{ m}^{-3}$; unimodal Vesicle Volume Distributions (VVDs, the volume fraction of
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21 245 the vesicles at their equivalent volume) with a main peak corresponding to bubbles with diameter of
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24 246 200-300 μm , and regular (continuous) trends in the cumulative Vesicle Size Distributions (CVSDs)
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26 247 (Fig. 4 and 5).

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28 248 b) dark, scoriaceous and moderately vesicular clasts (trachyte) with a mean density value of 800
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31 249 kg/m^3 ; ~~vesicles~~. Vesicles larger than those of the pumiceous rhyolites are also present and typically
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33 250 form a corona surrounding mineral fragments. With respect to the rhyolites, the dark scoriae show
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35 251 higher *VND* values, in the order of $7 \times 10^{11} \text{ m}^{-3}$. VVDs show multi-modal distributions with several
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37 252 primary modes ~~in correspondence of~~ corresponding to larger bubbles (main peaks at 200-300 μm and
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39 253 1200-1300 μm); CVSDs are characterized by irregular trends with a second peak towards the
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42 254 smaller bubbles (30–60 μm), also well-evident in the size frequency histogram (Fig. 4 and 5);

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44 255 c) banded clasts (rhyolite or trachyte), with intermediate textural parameters between white
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47 256 pumices and dark scoriae; ~~these~~. These intermediate clasts show sinuous-convoluted mm to cm-wide
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49 257 bands separated by sharp boundaries with colour and vesicular variations (Fig. 4 and 5). Vortical
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51 258 structures defined by bands of vesicles with different orientation may be recognized (Fig. 4).

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53 259 Vesicles of trachytic and rhyolitic clasts show similar ~~degree~~ degrees of deformation with size,
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55 260 except for the nearly undeformed larger bubbles ($> 800 \text{ m}$) recorded only in trachytes. These larger,
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58 261 sub-circular vesicles are located around crystals and deform the surrounding smaller bubbles, ~~which~~
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60 262 ~~result to be strained~~ (Fig. 5D).

5. Discussion

5.1 Depth and geometry of the ME reservoir

Our data indicate that the ME juvenile fraction is characterized by clasts of different glass composition, H₂O, Cl, F, S and CO₂ abundances, textural features, and VVDs and CSVDs patterns. The plots of Fig. 3 clearly show an increase of H₂O, F and Cl concentrations with the degree of evolution. This behaviour is consistent with a fractional crystallization process of observed crystal phases and confirm, according to independent petrological data, that trachytes and rhyolites are related by dominant fractionation processes (Yi *et al.*, 2021) with the rhyolites representing the most differentiated volatile-rich liquids. The compositional gap observed between trachytes and rhyolites has been attributed to the occurrence of two distinct magma batches at different depth (Zhang *et al.*, 2018; Pan *et al.*, 2017), whereas Lee *et al.* (2021) propose a single, zoned magma chamber. Recent models of long-lived magma chambers (Garg *et al.*, 2019) show that endmember magmas stored in a zoned, large single reservoir may maintain their original composition for long time, and mixing/mingling processes may be related to syn-eruptive processes. The observed limited mingling between trachytes and rhyolites during ME suggests a restricted syn-eruptive interaction between the two magmas, as also suggested by Yi *et al.* (2021) based on geochemical data. Also, the observed intermediate glass compositions in the distal tephra and bi-modal compositions in the proximal deposits indicate, according to Chen *et al.* (2016), that the trachytic and rhyolitic magmas underwent a restricted, syn-eruptive interaction. A mechanism of replenishment of the ME rhyolitic reservoir by the arrival of 'fresh', new trachytic melt from a deeper magma chamber is not supported by our data, which show that the trachyte is relatively phenocrystal-rich (up to about 30 vol.%). This crystallinity, along with the occurrence of microcrystals in the groundmass and a relatively low porosity, suggests that the ME trachytes represents a poorly buoyant, less evolved crystal-rich magma possibly located at the bottom of the reservoir. This condition is not exclusive of This conclusion is supported by zircon crystallization ages of the ME trachyte (Zou *et al.*, 2021), which yield multiple age populations of ~1

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3 289 ka, 10 ka and 100 ka. These data indicate the occurrence of long-lived, crystal-rich storage zone.
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6 290 Therefore, we exclude that this trachytic magma may have triggered the ME. The compositional gap
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8 291 observed between the ME trachytes and rhyolites is not unique to the ME magmatic system, but it
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10 292 has been inferred from deposits of other large-scale eruptions, e.g., the 22ka old ‘Pomici di Base’
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12 293 Plinian eruption at Somma-Vesuvius (Italy) (Pappalardo *et al.*, 2018; Buono *et al.*, 2020). To better
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14 294 constrain the ‘single’ chamber hypothesis for ME, the volatile (H₂O and CO₂) concentrations
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16 295 measured on the matrix-glasses of the ME trachytes and rhyolites have been converted in saturation
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18 296 pressures by using available solubility models (Liu *et al.*, 2005; Papale *et al.*, 2006) and assuming,
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20 297 according to the available geochemical data (Iacovino *et al.*, 2016), that the magma is saturated. The
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22 298 results are reported in Fig. 6 and indicate a magma accumulation region located between 200-100
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24 299 MPa for both trachyte and rhyolite without significant differences in pressure. Although this pressure
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26 300 range represents minimum values because of the possible CO₂ release during the ME, however, our
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28 301 results are fully consistent with independent estimates based on melt and fluid inclusions in
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30 302 phenocrysts of the ME products, which give values of 100-170 MPa (Andreeva *et al.*, 2019).
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32 303 Therefore, our pressure estimates indicate a single ME magma reservoir. Also, the results by
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34 304 Andreeva *et al.* (2019) indirectly substantiate our assumption about the saturation of the ME magmas
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36 305 during the eruptive event. Assuming an average density of the metamorphic basement of the
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38 306 Changbaishan volcano of 2700 kg/m (Chi *et al.*, 2013), the depth of the reservoir deduced by the
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40 307 pressure values in Fig. 6 is between 7.5 and 3.7 km. These depth range overlaps the shallower and
41
42 308 deeper boundaries of the low density and low seismic velocity anomalies recorded below the volcano
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44 309 by modelling of gravity and seismic data (Choi *et al.*, 2013; Zhang *et al.*, 2002a,b). In addition, a low
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46 310 resistivity zone has been detected by Qui *et al.* (2014) between 5 and 8 km depth; this depth range
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48 311 covers the 4 to 8 km reduction of S-wave velocities found below Changbaishan (Hammond *et al.*,
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50 312 2020). A petrological study on the evolution of the Changbaishan magmatism based on
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52 313 clinopyroxene-melt thermobarometers also suggests a single magma chamber for the Changbaishan
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54 314 trachytes and rhyolites including the products of ME located between 3 and 5 km depth, and the

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3 315 occurrence of a deeper, basaltic reservoir at 20-25 km depth (Lee *et al.*, 2021). As a result, we
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5 316 conclude that the magmatic system responsible for ME consisted in an about 3-4 km thick single
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8 317 reservoir located in the upper crust and, based on the available geophysical data, this reservoir is
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10 318 today characterized by the presence of melts and must be considered active. To better constrain the
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12 319 size of the ME reservoir, we determine the Changbaishan caldera area (19.6 km²) and consider the
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14 320 ME erupted volume (96 ± 19 km³; Horn and Schmincke, 2000). The resulting vertical extension of
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17 321 the ME reservoir is 4between 4.85 ± 1 km³ km, a value comparable to the 3.7 km deduced from our
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19 322 determination of the pressures calculated from solubility models. Therefore, assuming a cylindrical
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22 323 geometry for the ME reservoir with an area of the caldera of 19.6 km², we estimate a volume of the
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24 324 ME magma chamber of about 7894 km³ ± 20 km³, a value in the lower bound of those consistent with
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26 325 that obtained from independent volcanological data (Horn and Schmincke, 2000).
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30 31 327 5.2 Evidence of an external triggering mechanism for the ME

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33 328 Our data on vesicles of the ME products show that the presence of coarser modes in the VVDs
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35 329 of trachytic clasts can be partly attributed to heterogeneous bubble nucleation processes around
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38 330 phenocrysts, as clearly visible in the 3D images of dark scoriae (Figs. 4 and 5). This type of nucleation
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40 331 has been also detected in andesitic magmas (Pleše, *et al.*, 2018), where crystals act as preferred sites
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42 332 of bubble growth. In ME, the spherical, large bubbles testify an earliest bubble nucleation event
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45 333 occurred mainly during cooling and phenocryst crystallization in a chamber (second boiling); this
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47 334 evidence confirms the water (over)saturated nature of magmas according to geochemical model
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49 335 (Iacovino *et al.*, 2016), (Fig. 6). The rounded shape of bubbles indicates that expansion continued
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52 336 above the fragmentation level in the slowly cooled clast interiors (post-fragmentation expansion;
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54 337 Mitchell *et al.*, 2018). The higher *VNDs* associated to a second peak of small bubbles in CVSDs of
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56 338 the ME trachytes indicate the involvement of a later, superimposed vesicle generation rather than
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58 339 successive growth and coalescence of a single vesicle population (Pappalardo *et al.*, 2018; Liedl *et*
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60 340 *al.*, 2019). This could be related to bubble nucleation due to a fast decompression just below the

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3 341 fragmentation level (Toramaru, 2014; Mangan *et al.*, 2000), or to an addition of gas from a deeper
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5 342 source to the reservoir. The trachytic and rhyolitic ME glasses contain various amount of CO₂ (Fig.
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8 343 6) while data on melt inclusions (Iacovino *et al.*, 2006) show that the ME reservoir was CO₂-poor
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10 344 (CO₂ range from 0 in trachyte to 20 ppm in rhyolite) in the pre-eruptive stage, providing evidence for
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12 345 the lack of significant CO₂ dissolved in the trapped melts (see Fig. 6). Therefore, the carbon dioxide
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14 346 we detect in the rhyolitic and trachytic glasses (> 60 - 600 ppm) could be supplied by a source external
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17 347 to the ME reservoir and was probably injected just before the eruption. The sudden increase of
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19 348 pressure by a CO₂ flushing-type mechanism related to a source external to the magma chamber may
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21 349 potentially trigger volcanic eruptions (Caricchi *et al.*, 2018). In this framework, the CO₂ content of
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23 350 the fluid inclusions from Iacovino *et al.* (2016), which is virtually 0, abruptly increases in the glasses
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25 351 of both ME trachytes and rhyolites (Fig. 6) according to a trend compatible with a flushing mechanism
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27 352 and not with fractionation or magma mixing processes. We exclude crustal carbonates as a possible
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29 353 source of CO₂ because evidence of such lithologies is lacking in the xenoliths of ME and in the
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31 354 deposits of the preceding Changbaishan eruptions (Zhang *et al.*, 2018; Yi *et al.*, 2021). The source of
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33 355 CO₂ we record in the ME glasses could be a deeper, not erupted CO₂-rich basaltic magma or,
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35 356 according with the available geochemical information on the gas released at Changbaishan and
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38 357 surrounding areas as the Songliao basin, the carbonate ~~melts released to the asthenospheric mantle~~
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42 358 ~~from the 500 km deep stagnant slab and originated from subducted carbonates and organic~~
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45 359 ~~metasediments-rich component of the mantle~~ (Zhang *et al.*, 2015; Wei *et al.*, 2016; Liu *et al.*, 2018;
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47 360 Zhao *et al.*, 2021; Sun *et al.*, 2021) (Fig. 1B). Lacking evidences of a direct involvement of a basaltic
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49 361 magma in the ME deposits and in the last 0.04 Ma of activity at Changbaishan, we propose that ~~this~~
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52 362 ~~slab-derived~~ CO₂ upraises from two possible sources: a) a passively degassing unerupted basaltic,
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54 363 metasomatized melt stored in a reservoir at 20-25 km depth (Lee *et al.*, 2021) or underplated at
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56 364 mantle/crust interface at 30-35 km, as suggested by tomographic studies (Zhu *et al.*, 2019), and/or b)
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58 365 a carbonate-rich ~~melt~~melts stored ~~above~~in the mantle wedge ~~and consisting of mixed recycled~~
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366 ~~sedimentary carbonates and MORB-type basalts (Li et al., 2017)~~ (Fig. 1b). In ~~both~~all these cases, the

CO₂ upraising from depth accumulates at the base of the ME reservoir, which could be partly isolated from the surroundings because of a crystal-mush partly sealing its boundaries. According to a mechanism proposed by Vigneresse (2015) for the gas-crystal interaction in intrusive bodies, at crystallinity values > 0.5-0.75 a quasi-locked framework of crystals reduces the motion of accumulating gas and favour its storage in the mush and an increase in overpressure. The crystal mush may not sustain shear stress, and if the gas pressure increases unlocking the crystal framework, this latter destabilizes, and the gas quickly enters the reservoir, also favouring upward heat advection and rejuvenation of the whole system (Bachmann and Bergantz, 2006). Evidence of a crystal mush in the ME magmatic system are provided by (a) some clinopyroxene and plagioclases crystals with extremely variable age (≤ 6 ka to ≥ 23 ka; Kuritani *et al.*, 2020) and, (b) presence of zircons in the range 1 ka-100 ka in trachytes (Zou *et al.*, 2021), and (c) dissolution textures which can not be explained by magma mixing (Yi *et al.*, 2021). According to available experimental data on alkaline magmas (Giuffrida *et al.*, 2017), the input of CO₂ in a magmatic system induces an enrichment in Ca of pyroxenes, a feature recorded in the microlites of the ME trachytes (Fig. 2B). The injection of deep CO₂ in the ME reservoir can destabilize the whole Changbaishan magmatic system and trigger ME.

5.3 Rupture conditions of the ME reservoir

To estimate the rupture conditions of the ME reservoir, we set the top of the reservoir at about 3.7 km depth (see above) and a density of the basement crustal rocks of 2700 kg/m³ (Choi *et al.*, 2013); the resulting lithostatic pressure P_L is about 98 MPa. In the following, we assume that the fluid pressure P_f is the pressure exerted by CO₂ pushing the crust above the ME reservoir. We assume an extensional-shear rupture mechanism following the Griffith's criterion and determine P_f required to activate shear failure and crack opening at 3.7 km depth. The condition for an extensional-shear failure mode is given by (Sibson, 2000):

$$4T \leq \sigma_1 - \sigma_3 \leq 5.66T(1)$$

$$P_f = \sigma_3 + [8T(\sigma_1 - \sigma_3) - (\sigma_1 - \sigma_3)^2] / 16T \quad (2)$$

where $\sigma_1 = P_L$ is the maximum stress, which is vertical in a normal stress regime, σ_3 is the horizontal least compressive stress and T is the tensile strength of the rocks. T varies between 14 and 8.5 MPa for intrusive and metamorphic rocks (Touloukian et al., 1981) and we select an average value $T = 10$ MPa. Using the above defined parameters, σ_3 is 49.7 ± 8.3 MPa and $P_f = 58.8 \pm 9.2$ MPa. The obtained values are in the range of those required for the rupture of silicic chambers (10 to 100 MPa; Manga and Brodsky, 2006). We conclude that the pressure increase due to CO_2 entering the ME reservoir was enough to produce the failure the overlying crustal rocks. The fluid pressure increase estimated by us is larger than the minimum horizontal stress and roughly half of the lithostatic stress.

5.4 The role of ~~slab-derived~~ mantle fluids in triggering the 2002-2006 unrest at Changbaishan and the relationships between the recent dynamics and the ME reservoir

The increase of CO_2 , He and $^3\text{He}/^4\text{He}$ ($R/R_a = 4.8$ in 2002 and $R/R_a = 6.6$ in 2006) in the emitted gas during the 2002-2006 unrest episode at Changbaishan (Xu et al., 2012) and the B isotopic values, which are compatible with fluids released from ~~the subducted Pacific plate (Zhao et al., 2019), indicate that fluids released from~~ a deep, metasomatic mantle source (Zhao et al., 2019). Such fluids may still enter the present-day ~ 4-8 km deep magmatic system. Otherwise, for example, the decay of U and Th in the magma chamber would result in continuously decreasing $^3\text{He}/^4\text{He}$ in the absence of the recharge of mantle-derived fluids or magmas (Moreira, 2013). This regional scale fluid release from the ~~Pacific stagnant slab mantle~~ is also supported by tomographic images (Lei et al., 2013; Ma et al., 2019), the huge CO_2 output in NE China including Changbaishan (2.1 Mt/yr), the $^3\text{He}/^4\text{He}$ values with R/R_a mostly between 3.5 and 6.5, and the $^{13}\text{C}_{\text{CO}_2}$ values between -5.6 ‰ and -13.7 ‰ (Zhao et al., 2021). At Changbaishan, a sudden decrease in the number of earthquakes between 2 and 7 km has been observed during the 2002-2006 unrest (Liu et al., 2021) (Fig. 7). This depth range is characterized by significant variations in geophysical parameters and overlaps that inferred by us for

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3 416 the ME magma reservoir (Fig. 7). We propose that this reduction in the number earthquakes and, in
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5 417 the same depth range, of the values of density, resistivity, and S-wave velocities in the upper crust is
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8 418 due to melts possibly representing a residuum of the ME magma chamber. Therefore, the ME
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10 419 reservoir is, at least in part, active and, according to the gas and water geochemistry, is flushed by
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12 420 CO₂-rich fluids of deep origin released from a deeper basaltic reservoir located in the lower crust or
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14 421 at the mantle/crust interface, or from the sub-lithospheric metasomatized mantle (Ham *et al.*, 2008).
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17 422 In this framework, the 7 to 11 km deep earthquakes could indicate the input of such deep fluids (and
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19 423 melt?) in the nearly solid crystal-mush bottom of the reservoir, while the shallower earthquakes (\leq
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21 424 km), which includes low-frequency events (Liu *et al.*, 2021), are related to the dynamics of the
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24 425 hydrothermal system likely destabilized from the transfer of such fluids from the reservoir to the
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26 426 shallower portions of the volcano. Accordingly, the earthquakes of the 2002-2006 unrest concentrated
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28 427 in the upper 2-3 km of the crust, where the hydrothermal system is stored (Zhang *et al.*, 2018), and
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31 428 just above the 2-6 km deep source of deformation modelled by levelling and GPS data (Xu *et al.*,
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33 429 2012). This conceptual model of the ME magmatic system provides constraints on the interpretation
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35 430 of the causative factors of past and, possibly, future unrest episodes. Our study shows how regional
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37 431 scale deep, ~~slab-derived~~mantle fluids may alter the stability of crustal reservoirs responsible for large
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40 432 scale eruptions. In intraplate and rift settings characterized by the continuous release of the deep CO₂,
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42 433 the effects of a such gas upwelling on intra-crustal magmatic reservoirs could represents an
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44 434 underestimated cause of destabilization. The geodynamic, deep processes discussed here must be
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47 435 considered in the interpretation of monitoring signals to properly decipher the dynamics of large,
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49 436 active magmatic systems.

53 438 6. Conclusions

55 439 The results of our analysis of the ME products may be summarized in the following points:

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58 440 1)The ME magmatic system consists in a single magma reservoir located at 3.7-7.5 km depth. This
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60 441 reservoir extends vertically for about 4 km and has a volume of 7894 km³.

2) The triggering mechanism of the ME eruption does not reflect processes internal to the reservoir but is related to the flushing of external carbon dioxide of deep, mantle origin. The arrival and progressive accumulation of deep carbon dioxide allowed the rupture of the ME reservoir. We exclude the arrival of a fresh and deeper trachytic magma into a rhyolitic magma reservoir ~~as~~ or ~~accumulation~~ the increase of fluid pressure due to fractional crystallization processes alsone as triggering mechanism of the eruption.

3) The fluid pressure induced by CO₂ flushing and required to destabilize the ME reservoir is in the order of 58.8±9.2 MPa at 3.7 km depth.

4)– The inferred depth of the ME reservoir is the same of that of some geophysical anomalies (resistivity, density, seismic wave velocities, hypocentral distribution of earthquakes of the 2002-2006 earthquakes). ~~During the~~ The 2002-2006 unrest reflects the destabilized of the residual reservoir of the ME by the arrival of CO₂-rich fluids from depth > 7-11 km and their transfer to the shallower (< 2-3 km depth) portions of the plumbing system of the volcano.

Our results highlight the role of regional scale processes as the upraising of slabmantle-derived fluids in NE China in the destabilization of shallow magma chambers associated to large scale eruptions. Geodynamic processes should be taken into account when interpreting unrest episodes at volcanoes.

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Figure captions

Figure 1. Geodynamic setting of Changbaishan volcano and 'Millenium' eruption stratigraphy. **(A)** Location of the Changbaishan volcano, depth of the earthquakes of the Pacific slab (white dashed lines; from Zhang *et al.*, 2018) and dispersion of 'Millenium' eruption rhyolitic fall deposit (isopaches in dashed yellow lines redrawn from Horn and Schmincke, 2000). **(B)** Simplified W-E tomography profile (from Ma *et al.*, 2019) extending from China to Japan and crossing the Changbaishan volcano. The main petrogenetic processes and their depth are summarized according to Xu *et al.* and Zhang *et al.*, 2015, 2018). **(C)** Topography of the Changbaishan volcano and dispersion of the ME pyroclastic flow deposits (from Pan *et al.*, 2017). Numbers indicate the sampling localities (samples are listed in the Supplementary Information). **(D)** Representative outcrop and rocks of the ME eruption fall deposit (sampling locality 2 in Fig. 1C).

Figure 2. Chemical features of ME rocks. **(A)** TAS (Total Alkali vs. Silica) diagram. Glass (matrix-glass): new data from this study, literature data from Pan *et al.*; melts inclusion (MI): data from Iacovino *et al.* (2016) **(B)** Composition of pyroxene phenocrysts and microlites from literature data.

Figure 3. Volatile content in ME rocks. **(A)** Silica vs. Cl, **(B)** silica vs. F and **(C)** silica vs. H₂O (EMPA data). **(D)** Normalized histograms for H₂O (TGA data). **(E)** Normalized histograms for CO₂ and **(F)** normalized histograms for S (CSA data) in glasses. Data from this study and Pan *et al.* (2017) and melts inclusions (MI; data from Iacovino *et al.*, 2016) in D,E,F are normalized to allow comparison between the different samples.

Figure 4. 3D images of ME rocks acquired through X-ray microtomography. Three-dimensional renderings of representative **(A)** white pumice, **(B)** dark scoriae and **(C)** banded scoria of ME. Diameter of cylinder is 5000 μm . The vesicles are black, the matrix-glass is dark-gray, minerals are

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715 light gray or white. Note the sinuous banding with deformed bubbles in the white pumice and the
716 large vesicles attached to crystals in the dark scoria.

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718 **Figure 5.** 3D textural features of ME rocks. (A) Vesicle volume distributions. (B) Cumulative
719 vesicle size distributions. (C) Normalized histogram of vesicles size. (D) Vesicle size vs. ratio
720 between the longest and shortest Feret diameter for representative samples. WP: white pumices (solid
721 and long dashed green lines), DS: dark scoriae (solid red lines), BC: banded clasts (short dashed
722 lines). For the sample K1-banded no chemical analyses are available.

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724 **Figure 6.** Magmatic processes recorded by H₂O vs. CO₂ contents. (A) H₂O vs. CO₂ concentration
725 in glasses (this study) and melt inclusions (data from Iacovino *et al.*, 2016) for the ME rhyolitic rocks.
726 (B) H₂O vs. CO₂ concentration in glasses (this study) and melt inclusions (data from Iacovino *et al.*,
727 2016) for the ME trachytic rocks. Saturation curves for rhyolite and trachyte at 800 °C were calculated
728 according to Liu *et al.* (2005) and Papale *et al.* (2006). The inset in (A) shows the processes that
729 typically control different H₂O-CO₂ trends.

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731 **Figure 7.** Seismicity of the 2002-2006 time period and interpretative model of the unrest. Epicentral
732 distribution of the earthquakes during the 2002-2006 unrest (data from Liu *et al.*, 2021), number of
733 earthquakes with depth and time evolution of the seismicity. The depth of the magma reservoir of
734 ME estimated in this study is reported as a vertical red bar. The main geophysical anomalies from
735 previous studies are reported as vertical blue bars (Choi *et al.*, 2013; Qiu *et al.*, 2014; Hammond *et*
736 *al.*, 2020). The arrows indicate the different processes involved during the unrest and discussed in the
737 text.

Supplementary Items

740 **Table S1. List of samples.** Rock samples collected from the different sampling sites (shown in Fig.
741 1C).

742 **Table S2. Geochemical data for White-Pumice.** Major elements, Cl and F concentrations in matrix-
743 glass through Electron Micro Probe Analyzer (EMPA).

744 **Table S3. Geochemical data for Dark-Scoria.** Major elements, Cl and F concentrations in matrix-
745 glass through Electron Micro Probe Analyzer (EMPA)

746 **Table S4. Geochemical data for Gray-Green-Scoria.** Major elements, Cl and F concentrations in
747 matrix-glass through Electron Micro Probe Analyzer (EMPA).

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748 **Table S5. Geochemical data for K1-White.** Major elements, Cl and F concentrations in matrix-
749 glass through Electron Micro Probe Analyzer (EMPA).

750 **Table S6. Volatile content in matrix-glasses.** H₂O data through thermogravimetric (TGA),
751 CO₂ and S through Carbon/Sulfur Analyses (CSA).

752 **Table S7. 3D textural data.** Analyses performed using X-ray computed microtomography.

753 **Figure. S1. 3D image of White-Pumice (caldera rim).** 3D volume rendering and 2D orthogonal
754 slices obtained through X-ray computed microtomography.

755 **Figure. S2. 3D image of Dark-Scoria (caldera rim).** 3D volume rendering and 2D orthogonal
756 slices obtained through X-ray computed microtomography.

757 **Figure. S3. 3D image of Gray-Green-Scoria (caldera rim).** 3D volume rendering and 2D
758 orthogonal slices obtained through X-ray computed microtomography.

759 **Figure. S4. 3D image of Sample3-White (caldera rim).** 3D volume rendering and 2D orthogonal
760 slices obtained through X-ray computed microtomography.

761 **Figure. S5. 3D image of Sample3-Dark (caldera rim).** 3D volume rendering and 2D orthogonal
762 slices obtained through X-ray computed microtomography.

763 **Figure. S6. 3D image of K1-Banded (caldera rim).** 3D volume rendering and 2D orthogonal slices
764 obtained through X-ray computed microtomography.

765 **Figure. S7. 3D image of Sample1-White (intermediate-distal area).** 3D volume rendering and 2D
766 orthogonal slices obtained through X-ray computed microtomography.

767 **Figure. S8. 3D image of CPF5 (intermediate-distal area).** 3D volume rendering and 2D orthogonal
768 slices obtained through X-ray computed microtomography.

769 **Figure. S9. 3D image of Western-Plain (intermediate-distal area).** 3D volume rendering and 2D
770 orthogonal slices obtained through X-ray computed microtomography.

771 **Figure. S10. 2D image of K1-White.** 2D (backscattered electron) images obtained through Scanning
772 Electron Microscope (SEM).

773 **Figure. S11. 2D image of K1-Dark.** 2D (backscattered electron) images obtained through Scanning
774 Electron Microscope (SEM).

775 **Figure. S12. 2D image of Sample3-Dark.** 2D (backscattered electron) images obtained through
776 Scanning Electron Microscope (SEM).

777 **Figure. S13. 2D image of Gray-Green-Scoria.** 2D (backscattered electron) images obtained through
778 Scanning Electron Microscope (SEM).

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3 1 **The role of CO₂ flushing in triggering the ‘Millennium’ eruption and recent unrests at**
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Abstract The impact of large-scale caldera-forming eruptions on our society and climate can be considerable. The triggering mechanisms of these eruptions and the instability of their magmatic systems are still elusive. Here we use X-ray tomographic microscopy, glass geochemistry and volatile element concentration data on the products of the 946 CE ‘Millennium’ eruption (ME) of Changbaishan volcano (China/North Korea) with the aim to identify the triggering mechanism of the eruption. ME emitted rhyolites and trachytes whose textural parameters suggest vesiculation events related to crystallization and magma ascent in the conduit, and to the arrival of new gas in the magmatic system. Solubility models show that the CO₂ and H₂O dissolved in the glass are consistent with a pressure of 100-200 MPa. Literature data from fluid inclusions in minerals indicate that the residing magma was CO₂ free before the eruption, whereas the CO₂ content in the glass reaches 600 ppm at the flash of the ME event. We find that a single, shallow magma reservoir localized between 7.5 and 3.7 km depth in which rhyolites occupies the top and trachytes the bottom is fully destabilized by the arrival of external CO₂-rich fluids. Such fluids are released from a deeper, carbonate-rich mantle source. Our results and those of independent geophysical data show that the ME magmatic system is still active, and the continuous upraising of fluids from depth may drive unrest episodes like that recorded in 2002-2006. Our findings elucidate the role of deep, mantle-derived fluids in driving large-scale explosive eruptions. We provide evidence that volcanic unrests may not mirror the internal dynamics of magmatic reservoirs.

Keywords: Changbaishan volcano; Plumbing system modeling; Triggering mechanism; CO₂ flushing; Storage depth

1. Introduction

Large-scale caldera-forming eruptions emit hundreds of km³ of magma and are among the most catastrophic natural events on Earth. Their effects on our society may be dramatic (Robock, 2000; Bryan, *et al.*, 2010); Brown *et al.*, 2014; Papale and Marzocchi, 2019). In the last 10000 years, 17

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3 58 eruptions with magnitude $M \geq 7$ have been recognized with at least 2 events occurred in the last 1000
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5 59 years (Croweller *et al.*, 2012; Oppenheimer *et al.*, 2017; Newhall *et al.*, 2018): the 1815 CE, $M = 7$
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7 60 eruption at Tambora, Indonesia, and the 946 CE, $M = 7.4$ ($M = 6.4 \div 7.2$ following Yang *et al.*, 2021)
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9 61 ‘Millennium’ eruption at Changbaishan volcano, China/North Korea. The knowledge of the geometry
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11 62 of the magmatic system associated to eruptions of a such size and of their triggering mechanisms is
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13 63 crucial to appropriately understand the monitoring signals during unrest episodes and assess the
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15 64 volcanic hazard (Acocella *et al.*, 2015). However, two still debated questions on large-scale eruptions
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17 65 concern (a) the occurrence of a huge, single magma chamber or of different reservoirs at different
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19 66 depth (Jellinek *et al.*, 2003; Cashman and Giordano, 2014; Kruger and Latypov, 2020). and (b) the
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21 67 mechanisms leading to eruption. Magma mixing, buoyancy (Caricchi *et al.*, 2014; Malfait *et al.*, 2014;
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23 68 Bergantz *et al.*, 2015), variations in volatile and crystal cargo content (Wark *et al.*, 2007), far-field
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25 69 tectonic stress (Costa *et al.*, 2016; Cabaniss *et al.*, 2018), and gas injection with dislocation and/or
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27 70 melting of the crystal-mush (Bachmann and Bergantz, 2006; Parmigiani *et al.*, 2014) have been
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29 71 proposed as leading mechanisms. The above summarized issues point out that our comprehension of
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31 72 large-scale magmatic systems is limited. Here we present X-ray tomographic microscopy textural and
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33 73 geochemical (glass composition and dissolved H_2O , CO_2 , S, F and Cl) data on the pumices and scoriae
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35 74 of the 946 CE ‘Millennium’ eruption (hereafter ME) at Changbaishan, an intraplate volcano at the
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37 75 China/North Korea border characterized by a 5 km wide summit caldera (Fig. 1A). We reconstruct
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39 76 the magma storage conditions and degassing processes of ME, calculate the depth of the reservoir,
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41 77 and recognize the roof rupture mechanism. We show that the ME magmatic system is still active and
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43 78 periodically shaken by the injection of mantle-derived fluids. We explain the signals of the 2002-
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45 79 2006 unrest episode at Changbaishan as due to the upraising of these fluids and focus on their role in
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47 80 the triggering mechanism of large-scale caldera forming eruptions. Our results provide a new
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49 81 perspective on the instability mechanisms of large magmatic systems, their link with larger scale
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51 82 geodynamic processes, i.e. deep degassing, with obvious implications for the volcano monitoring
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53 83 strategies and volcanic hazard assessment at calderas.

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2. Geodynamic and volcanological setting and the 946 CE ‘Millennium’ eruption

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Changbaishan volcano is located west of the Japan trench above the 500 km deep stagnant slab of the Pacific subduction (Fig. 1B; Lei *et al.*, 2013; Zhang *et al.*, 2018). Lei *et al.* (2013) detect a low velocity zone at 400 km depth possibly reflecting the fluid release and dehydration of the subducted Pacific slab. Changbaishan started its activity ~5 Ma ago with eruptions fed by basaltic, and later trachytic, magmas; in the last 0.04 Ma, pre-caldera silicic lava flows and caldera-forming eruptions occurred including ME (Zhang *et al.*, 2018; Pan *et al.*, 2020). Minor eruptions are postulated in 1403 CE, 1668 CE and 1702 CE (Sun *et al.*, 2017). However, Pan *et al.* (2017) report that the deposits attributed to these historical events represent the final phase of the ME. Changbaishan volcano suffered an unrest episode between 2002 and 2006 with changes in gas geochemistry, ground uplift and increase in the seismic rate (Xu *et al.*, 2012). CO₂-rich degassing areas and hot water emissions are widespread on Changbaishan with CO₂ discharge values up to 9.4×10^5 t/yr (Zhao *et al.*, 2021). According to the available geochemical data, such fluids are released from recycled carbonates and organic metasediments metasomatizing the mantle (Fig. 1B; Zhang *et al.*, 2015; Hahm *et al.*, 2008; Wei *et al.*, 2016; Xu *et al.*, 2020). A widespread release of CO₂ of mantle origin ($\delta^{13}\text{C} = -5.5 \pm 2.5\%$; He with R/Ra between 3.21 and 4.96) also characterizes other, large non-volcanic areas in NE China, e.g. the Songliao basin located 200 km north of Changbaishan (Liu *et al.*, 2018). Here, 146 wells distributed over an area of about 33700 km² contain a CO₂ percentage between 6 and 99%, testifying the regional scale accumulation and degassing of CO₂ from the mantle in NE China (Zhang *et al.*, 2018; 2020).

ME of Changbaishan emitted 96 ± 19 km³ (Dense Rock Equivalent, DRE = 24 ± 5 km³) of pyroclastics (Horn and Schmincke, 2000). Yang *et al.* (2021) report a volume of 40–98 km³, VEI = 6 and M = 6.4 ÷ 7.2. The column height was estimated >25 km and the fall deposits show an eastward dispersion with ashes found in Japan Sea, Japan mainland, Eastern Russia, and Greenland (Sun *et al.*, 2014; McLean *et al.*, 2016). ME deposits consist of an extensive white, nearly aphyric, rhyolitic

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3 110 pumice fallout and ignimbrite (95 vol.% of tephra), overlain by a fallout of dark, phenocryst-rich
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5 111 (30% vol.% of crystals), trachytic scoriae distributed on the crater rim and northeastern flank of
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8 112 Changbaishan (Machida *et al.*, 1990; Pan *et al.*, 2017, 2020; Yi *et al.*, 2021) (Fig. 1, C and D).
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10 113 Subordinates mingled rhyolite-trachyte clasts are interpreted as the result of the syn-eruptive
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12 114 interaction between the two magmas in the conduit (Pan *et al.*, 2017; Yi *et al.*, 2021). Although the
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14 115 rhyolite results from the fractionation of the trachytic magma, the geometry of the magmatic system
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17 116 is debated. Two models have been proposed: a large, single magma chamber (Iacovino *et al.*, 2016)
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19 117 or two separated sill-like reservoirs occupied by different but consanguineous trachytic and rhyolitic
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26 120 **3. Analytical methods**

28 121 *3.1 Rock samples*

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31 122 The examined ME rocks are rhyolitic pumices and trachytic scoriae, collected from proximal
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33 123 and distal outcrops of basal fallout and ignimbrite as well as upper fallout deposit, respectively.
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35 124 Sampling sites are summarized in Fig. 1C. Particularly, representative samples were selected based
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38 125 on the collected juvenile component by Yi *et al.* (2021) as these authors systematically analyzed the
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40 126 petrography, whole-rock chemistry, Sr-Nd isotopes, and minerals of pumices and scoriae. Thus these
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42 127 data constitute a robust background for our new textural and chemical analyses.
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45 128 Particularly, most of the samples (9 samples: three from yellow pumice fallout, three from dark
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47 129 scoria fallout and three from gray/green pumices fallout) come from the proximal outcrops where the
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49 130 stratigraphic relationship between the different eruptive units is well preserved (Yi *et al.*, 2021).
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51 131 However, two samples from distal fallout and one from ignimbrite deposits were also selected for
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54 132 comparison. Pumice and scoria samples are analysed by Electron Micro Probe Analyzer (EMPA) for
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56 133 major elements, Cl and F concentrations in matrix-glasses. H₂O as well as CO₂ and S contents are
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58 134 measured on matrix-glasses fragments by thermogravimetric (TGA) and Carbon/Sulfur Analyses
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60 135 (CSA), respectively. Samples are also inspected through Scanning Electron Microscope (SEM) and

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3 136 microtomographic analysis. Details on the samples and the results of the above summarized analyses
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5 137 are reported in the Supplementary data.
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10 139 *3.2 EMPA and SEM analyses*

12 140 EMPA analyses have been performed at the HP-HT Laboratory of Experimental Volcanology
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14 and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome (Italy), using
15 141 a Jeol-JXA8200 Electron Micro Probe Analyzer equipped with five wavelength dispersive
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17 142 spectrometers. Samples were analyzed under high vacuum conditions, using an accelerating voltage
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19 143 of 15 kV. The electron beam current was set at 7.5nA. Elemental counting times were 10 s on the
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21 144 peak and 5 s on background positions. Corrections for inter-elemental effects were made using a ZAF
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23 (Z: atomic number; A: absorption; F: fluorescence) routine. For each analysis, a defocused beam was
24 145
25 used to minimize losses of alkalis and volatiles, which were counted first to avoid diffusion effects.
26 146
27 The following standards have been adopted for the various chemical elements: jadeite (Si and Na),
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29 corundum (Al), forsterite (Mg), andradite (Fe), rutile (Ti), orthoclase (K), barite (Ba), Celestine (S),
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31 fluorite (F), apatite (P and Cl), and spessartine (Mn). Data reduction was carried out using ZAF4/FLS
32 149
33 software by Link Analytical. Accuracy was better than 1–5% except for elements with abundances
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35 below 1 wt.%, for which accuracy was better than 5–10%. Samples were also inspected through
36 151
37 backscattered electron (BSE) 2D images collected using a SEM JEOL JSM-6500F and operating at
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39 15 kV at INGV in Rome.
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49 156 *3.3 Thermogravimetric (TGA) and Carbon/Sulfur (CSA) analyses*

51 157 The collected juvenile samples, in particular the pumices, were carefully treated and examined.
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53 First of all, they were stored overnight in a bath of H₂O₂ (aqueous solution at 20%) to remove organic
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55 materials. After this treatment, the samples were left in air to dry for 24 h and stored overnight in a
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57 drying box at 35–40°C, to release also the water possibly absorbed from the glass surface. The samples
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60 161 were then cut by a low-speed diamond saw and the inner pattern of bubbles of each sample was

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162 examined to select the samples more suitable for analyses. The bubble size pattern exposed on the
163 cut area helps in tracing the history of the nucleation event(s) that occurred before and during magma
164 cooling. A pumice showing bigger vesicles in the center and smaller ones toward its rim surface was
165 not considered for further investigations because such bubble pattern indicates that the vesiculation
166 process continued after magma fragmentation during the pumice cooling. Only the pumices showing
167 a homogeneous distribution of vesicles were further considered for the analyses. The juvenile samples
168 were cut in a way to preserve only their core. In the case of samples containing phenocrysts (up to 2
169 mm), these were manually removed before measurements.

170 Since the samples were too vesiculated and fragile to prepare as doubly polished thin sections
171 for Fourier Transform Infrared Spectroscopy (FTIR) measurements, direct methods as TGA and CSA
172 analyses were chosen to analyse the volatile contents of the matrix-glass samples. The measurements
173 were performed at the Institute of Mineralogy of the University of Göttingen. Water contents were
174 determined by TGA by using a Setaram TM TGA92. following the standard procedure described in
175 Schmidt and Behrens (2008) and Behrens *et al.* (2009), about 20 mg of sample per measurement were
176 filled into a Pt crucible and suspended to a balance in a graphite tube furnace. During a typical
177 measurement, the sample is heated to 1200°C at a rate of 10°C/min in He flow and cooled at a rate of
178 30°C/min after a 30 min dwell time. The mass of the (dehydrating) sample is continuously recorded.
179 The buoyancy of the suspended crucible and sample may change, for instance, with changing
180 temperature. Once a day, a blank measurement was recorded, consisting of an additional heating and
181 cooling cycle performed on an already measured and consequently degassed sample. Blank
182 measurements were subtracted from the sample signal in order to eliminate the effect of buoyancy on
183 crucible and sample. For each sample, three-to-six thermogravimetric analyses were performed. The
184 determination of the CO₂ and S content on matrix-glass samples was performed with an Elementar
185 TM Inductar CS Cube, following the procedure described by Behrens *et al.* (2009). During a typical
186 measurement, 0.5g Fe and 2g W are inserted together with 35 to 50 mg of crushed sample material
187 into a ceramic crucible. The mixture is burned in an induction furnace at roughly 2000°C in an oxygen

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3 188 stream and the released CO₂ is measured by an Infrared (IR) cell. A typical day of analyses starts with
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5 189 a series of blank measurements without sample (0.5g Fe + 2g W only) followed by a series of
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8 190 measurements of steel standards with known CO₂ and S contents. The blank and the standard
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10 191 measurements are needed to daily calibrate the CSA and correct the analyzed experimental samples
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12 192 accordingly. TGA and CSA results show water and S contents lower or in the range of the values
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15 193 measured on not degassed melt inclusions, except for CO₂ that is absent in melt inclusions measured
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17 194 by (Iacovino *et al.*, 2016).

21 196 3.4 Microtomographic analysis

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24 197 Microtomographic analyses have been performed using a Carl Zeiss Xradia Versa-410 3D X-
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26 198 ray microscope at INGV-Osservatorio Vesuviano in Napoli (Italy). Samples of diameter 1.5-3 cm
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28 199 were scanned in absorption mode, acquiring 4001 projections over a 360° rotation at 90-80 KV and
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31 200 8-7 W with objective 4x. The resulting nominal voxel (volumetric pixel) size is 4.48 μm. The
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33 201 tomographic reconstruction was achieved through a filtered back-projection algorithm using XRM
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35 202 Reconstructor software, thus producing a stack of 967 cross-sectional, grey-scale digital images.
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38 203 Image analyses were performed by using the Avizo (FEI) program and following the procedure
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40 204 described by Liedl *et al.* (2019).

45 206 4. Results

47 207 4.1 Petrology and geochemistry of ME rocks

49
50 208 The glass-matrix compositions range from trachyte to rhyolite (comendite) (Fig. 2A). A clear
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52 209 compositional gap of about 5-10 wt% SiO₂ separates these two endmembers. Yi *et al.* (2021) find
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54 210 minor but ubiquitous mingled/mixed clasts in the ME products with SiO₂ ranging from 70 to 75 wt%
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57 211 on the basis of whole-rock analysis. These values only partially fill the compositional gap of observed
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59 212 SiO₂ in the glasses.
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3 213 The rhyolitic pumices are phenocryst-poor (crystal content: ~0–10 vol.%, K-feldspar >
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5 214 clinopyroxene > olivine > quartz>Fe-Ti oxides>apatite), and show a glassy, vesicle-rich matrix (bulk
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8 215 porosity % between 71 and 73). By contrast, the trachytic scoriae are moderately vesiculated and
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10 216 porphyritic, with up to 30 vol.% crystals (K-feldspar > clinopyroxene > olivine > Fe-Ti oxide >
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12 217 quartz> apatite) scattered in a dark microlite-bearing matrix-glass with porosity of 64% (see figures
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15 218 in the Supplementary data). Multi-banded clasts are also present and composed of dark, less vesicular
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17 219 and white vesicular bands; the porosity is between 68 to 73%. EMPA analyses indicate that the
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19 220 different bands in a single clast have homogenous trachytic or rhyolitic composition. K-feldspar
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21 221 phenocrysts show similar compositions in trachyte and rhyolite (Li *et al.* 2008). According to Yi *et*
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24 222 *al.* (2021). Clinopyroxene phenocrysts are characterized by a decrease in Mg and Ca contents from
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26 223 trachyte to rhyolite; microlites have higher Ca content than phenocrysts, especially marked in
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28 224 trachytes (Fig. 2B).

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31 225 Water, CO₂ and Cl are enriched in the sub-aphyric rhyolitic matrix-glasses (from 1.07 to 4.38
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33 226 wt%, from 73 to 618 ppm and > 0.35 wt%, respectively) with respect to the trachytes (from 0.15 to
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35 227 1.42 wt%, from 58 to 438 ppm and < 0.2 wt%, respectively). F and S abundances are more scattered
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38 228 in both compositions (rhyolite: F from 0 to 0.25 wt% and S from 12 to 165 ppm; trachyte: F from 0
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40 229 to 0.25 wt% and S from 14, despite a datum at 1.6 ppm, to 195 ppm) (Fig. 3).

42 230 43 44 231 4.2 Microstructure

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47 232 The three-dimensional (3D) rock microstructure is investigated by X-ray microtomography on
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49 233 representative ME samples. Details and results are provided in the Materials and Methods section and
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51 234 in the Supplementary data. Based on their textural features, the analyzed samples can be separated
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54 235 into three groups as follows:

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56 236 a) white pumiceous clasts (rhyolite) with a mean density value of 700 kg/m³ containing rounded
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58 237 vesicles, although minor bands of elongated vesicles can be present. These clasts display Vesicle
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60 238 Number Density values (*VND*, the number of vesicles in each size class per unit melt or bulk volume)

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3 239 in the order of $3 \times 10^{11} \text{ m}^{-3}$; unimodal Vesicle Volume Distributions (VVDs, the volume fraction of
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5 240 the vesicles at their equivalent volume) with a main peak corresponding to bubbles with diameter of
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8 241 200-300 μm , and regular (continuous) trends in the cumulative Vesicle Size Distributions (CVSDs)
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10 242 (Fig. 4 and 5).

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12 243 b) dark, scoriaceous and moderately vesicular clasts (trachyte) with a mean density value of 800
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14 244 kg/m^3 . Vesicles larger than those of the pumiceous rhyolites are also present and typically form a
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17 245 corona surrounding mineral fragments. With respect to the rhyolites, the dark scoriae show higher
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19 246 VND values, in the order of $7 \times 10^{11} \text{ m}^{-3}$. VVDs show multi-modal distributions with several primary
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21 247 modes corresponding to larger bubbles (main peaks at 200-300 μm and 1200-1300 μm). CVSDs are
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24 248 characterized by irregular trends with a second peak towards the smaller bubbles (30–60 μm), also
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26 249 well-evident in the size frequency histogram (Fig. 4 and 5);

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28 250 c) banded clasts (rhyolite or trachyte), with intermediate textural parameters between white
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31 251 pumices and dark scoriae. These intermediate clasts show sinuous-convoluted mm to cm-wide bands
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33 252 separated by sharp boundaries with colour and vesicular variations (Fig. 4 and 5). Vortical structures
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35 253 defined by bands of vesicles with different orientation may be recognized (Fig. 4).

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37 254 Vesicles of trachytic and rhyolitic clasts show similar degrees of deformation with size, except
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40 255 for the nearly undeformed larger bubbles ($> 800 \mu\text{m}$) recorded only in trachytes. These larger, sub-
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42 256 circular vesicles are located around crystals and deform the surrounding smaller bubbles (Fig. 5D).

43 44 45 257 46 47 258 **5. Discussion**

48 49 259 *5.1 Depth and geometry of the ME reservoir*

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51 260 Our data indicate that the ME juvenile fraction is characterized by clasts of different glass
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54 261 composition, H_2O , Cl, F, S and CO_2 abundances, textural features, and VVDs and CSVDs patterns.
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56 262 The plots of Fig. 3 clearly show an increase of H_2O , F and Cl concentrations with the degree of
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58 263 evolution. This behaviour is consistent with a fractional crystallization process of observed crystal
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60 264 phases and confirm, according to independent petrological data, that trachytes and rhyolites are

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related by dominant fractionation processes (Yi *et al.*, 2021) with the rhyolites representing the most differentiated volatile-richer liquids. The compositional gap observed between trachytes and rhyolites has been attributed to the occurrence of two distinct magma batches at different depth (Zhang *et al.*, 2018; Pan *et al.*, 2017), whereas Lee *et al.* (2021) propose a single, zoned magma chamber. Recent models of long-lived magma chambers (Garg *et al.*, 2019) show that endmember magmas stored in a zoned, large single reservoir may maintain their original composition for long time, and mixing/mingling processes may be related to syn-eruptive processes. The observed limited mingling between trachytes and rhyolites during ME suggests a restricted syn-eruptive interaction between the two magmas, as also suggested by Yi *et al.* (2021) based on geochemical data. Also, the observed intermediate glass compositions in the distal tephra and bi-modal compositions in the proximal deposits indicate, according to Chen *et al.* (2016), that the trachytic and rhyolitic magmas underwent a restricted, syn-eruptive interaction. A mechanism of replenishment of the ME rhyolitic reservoir by the arrival of 'fresh', new trachytic melt from a deeper magma chamber is not supported by our data, which show that the trachyte is relatively phenocrystal-rich (up to about 30 vol.%). This crystallinity, along with the occurrence of microcrystals in the groundmass and a relatively low porosity, suggests that the ME trachytes represents a poorly buoyant, less evolved crystal-rich magma possibly located at the bottom of the reservoir. This conclusion is supported by zircon crystallization ages of the ME trachyte (Zou *et al.*, 2021), which yield multiple age populations of ~1 ka, 10 ka and 100 ka. These data indicate the occurrence of long-lived, crystal-rich storage zone. Therefore, we exclude that this trachytic magma may have triggered the ME. The compositional gap observed between the ME trachytes and rhyolites is not unique to the ME magmatic system, but it has been inferred from deposits of other large-scale eruptions, e.g., the 22ka old 'Pomice di Base' Plinian eruption at Somma-Vesuvius (Italy) (Pappalardo *et al.*, 2018; Buono *et al.*, 2020). To better constrain the 'single' chamber hypothesis for ME, the volatile (H₂O and CO₂) concentrations measured on the matrix-glasses of the ME trachytes and rhyolites have been converted in saturation pressures by using available solubility models (Liu *et al.*, 2005; Papale *et al.*, 2006) and assuming, according to the

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3 291 available geochemical data (Iacovino *et al.*, 2016), that the magma is saturated. The results are
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5 292 reported in Fig. 6 and indicate a magma accumulation region located between 200-100 MPa for both
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8 293 trachyte and rhyolite without significant differences in pressure. Although this pressure range
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10 294 represents minimum values because of the possible CO₂ release during the ME, however, our results
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12 295 are fully consistent with independent estimates based on melt and fluid inclusions in phenocrysts of
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14 296 the ME products, which give values of 100-170 MPa (Andreeva *et al.*, 2019). Therefore, our pressure
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17 297 estimates indicate a single ME magma reservoir. Also, the results by Andreeva *et al.* (2019) indirectly
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19 298 substantiate our assumption about the saturation of the ME magmas during the eruptive event.
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21 299 Assuming an average density of the metamorphic basement of the Changbaishan volcano of 2700
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24 300 kg/m (Chi *et al.*, 2013), the depth of the reservoir deduced by the pressure values in Fig. 6 is between
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26 301 7.5 and 3.7 km. These depth range overlaps the shallower and deeper boundaries of the low density
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28 302 and low seismic velocity anomalies recorded below the volcano by modelling of gravity and seismic
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31 303 data (Choi *et al.*, 2013; Zhang *et al.*, 2002a,b). In addition, a low resistivity zone has been detected
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33 304 by Qui *et al.* (2014) between 5 and 8 km depth; this depth range covers the 4 to 8 km reduction of S-
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35 305 wave velocities found below Changbaishan (Hammond *et al.*, 2020). A petrological study on the
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37 306 evolution of the Changbaishan magmatism based on clinopyroxene-melt thermobarometers also
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40 307 suggests a single magma chamber for the Changbaishan trachytes and rhyolites including the products
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42 308 of ME located between 3 and 5 km depth, and the occurrence of a deeper, basaltic reservoir at 20-25
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44 309 km depth (Lee *et al.*, 2021). As a result, we conclude that the magmatic system responsible for ME
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47 310 consisted in an about 3-4 km thick single reservoir located in the upper crust and, based on the
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49 311 available geophysical data, this reservoir is today characterized by the presence of melts and must be
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51 312 considered active. To better constrain the size of the ME reservoir, we determine the Changbaishan
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54 313 caldera area (19.6 km²) and consider the ME erupted volume (96 ± 19 km³; Horn and Schmincke,
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56 314 2000). The resulting vertical extension of the ME reservoir is between 4.85 ± 1 km³ km, a value
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58 315 comparable to the 3.7 km deduced from our determination of the pressures calculated from solubility
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60 316 models. Therefore, assuming a cylindrical geometry for the ME reservoir with an area of the caldera

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3 317 of 19.6 km², we estimate a volume of the ME magma chamber of about 94 km³ ± 20 km³, a value
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5 318 consistent with that obtained from independent volcanological data (Horn and Schmincke, 2000).
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10 320 5.2 Evidence of an external triggering mechanism for the ME

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12 321 Our data on vesicles of the ME products show that the presence of coarser modes in the VVDs
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14 322 of trachytic clasts can be partly attributed to heterogeneous bubble nucleation processes around
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16 323 phenocrysts, as clearly visible in the 3D images of dark scoriae (Figs. 4 and 5). This type of nucleation
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18 324 has been also detected in andesitic magmas (Pleše, *et al.*, 2018), where crystals act as preferred sites
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20 325 of bubble growth. In ME, the spherical, large bubbles testify an earliest bubble nucleation event
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22 326 occurred mainly during cooling and phenocryst crystallization in a chamber (second boiling); this
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24 327 evidence confirms the water (over)saturated nature of magmas according to geochemical model
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26 328 (Iacovino *et al.*, 2016), (Fig. 6). The rounded shape of bubbles indicates that expansion continued
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28 329 above the fragmentation level in the slowly cooled clast interiors (post-fragmentation expansion;
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30 330 Mitchell *et al.*, 2018). The higher VNDs associated to a second peak of small bubbles in CVSDs of
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32 331 the ME trachytes indicate the involvement of a later, superimposed vesicle generation rather than
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34 332 successive growth and coalescence of a single vesicle population (Pappalardo *et al.*, 2018; Liedl *et*
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36 333 *al.*, 2019). This could be related to bubble nucleation due to a fast decompression just below the
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38 334 fragmentation level (Toramaru, 2014; Mangan *et al.*, 2000), or to an addition of gas from a deeper
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40 335 source to the reservoir. The trachytic and rhyolitic ME glasses contain various amount of CO₂ (Fig.
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42 336 6) while data on melt inclusions (Iacovino *et al.*, 2006) show that the ME reservoir was CO₂-poor
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44 337 (CO₂ range from 0 in trachyte to 20 ppm in rhyolite) in the pre-eruptive stage, providing evidence for
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46 338 the lack of significant CO₂ dissolved in the trapped melts (see Fig. 6). Therefore, the carbon dioxide
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48 339 we detect in the rhyolitic and trachytic glasses (> 60 - 600 ppm) could be supplied by a source external
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50 340 to the ME reservoir and was probably injected just before the eruption. The sudden increase of
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52 341 pressure by a CO₂ flushing-type mechanism related to a source external to the magma chamber may
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54 342 potentially trigger volcanic eruptions (Caricchi *et al.*, 2018). In this framework, the CO₂ content of

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3 343 the fluid inclusions from Iacovino *et al.* (2016), which is virtually 0, abruptly increases in the glasses
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5 344 of both ME trachytes and rhyolites (Fig. 6) according to a trend compatible with a flushing mechanism
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8 345 and not with fractionation or magma mixing processes. We exclude crustal carbonates as a possible
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10 346 source of CO₂ because evidence of such lithologies is lacking in the xenoliths of ME and in the
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12 347 deposits of the preceding Changbaishan eruptions (Zhang *et al.*, 2018; Yi *et al.*, 2021). The source of
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14 348 CO₂ we record in the ME glasses could be a deeper, not erupted CO₂-rich basaltic magma or,
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17 349 according with the available geochemical information on the gas released at Changbaishan and
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19 350 surrounding areas as the Songliao basin, the carbonate-rich component of the mantle (Zhang *et al.*,
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21 351 2015; Wei *et al.*, 2016; Liu *et al.*, 2018; Zhao *et al.*, 2021; Sun *et al.*, 2021) (Fig. 1B). Lacking
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23 352 evidences of a direct involvement of a basaltic magma in the ME deposits and in the last 0.04 Ma of
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25 353 activity at Changbaishan, we propose that CO₂ upraises from two possible sources: a) a passively
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27 354 degassing unerupted basaltic, metasomatized melt stored in a reservoir at 20-25 km depth (Lee *et al.*,
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29 355 2021) or underplated at mantle/crust interface at 30-35 km, as suggested by tomographic studies (Zhu
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31 356 *et al.*, 2019), and/or b) a carbonate-rich melts stored in the mantle wedge and consisting of mixed
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33 357 recycled sedimentary carbonates and MORB-type basalts (Li *et al.*, 2017) (Fig. 1b). In all these cases,
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35 358 the CO₂ upraising from depth accumulates at the base of the ME reservoir, which could be partly
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37 359 isolated from the surroundings because of a crystal-mush partly sealing its boundaries. According to
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39 360 a mechanism proposed by Vigneresse (2015) for the gas-crystal interaction in intrusive bodies, at
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41 361 crystallinity values > 0.5-0.75 a quasi-locked framework of crystals reduces the motion of
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43 362 accumulating gas and favour its storage in the mush and an increase in overpressure. The crystal mush
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45 363 may not sustain shear stress, and if the gas pressure increases unlocking the crystal framework, this
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47 364 latter destabilizes, and the gas quickly enters the reservoir, also favouring upward heat advection and
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49 365 rejuvenation of the whole system (Bachmann and Bergantz, 2006). Evidence of a crystal mush in the
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51 366 ME magmatic system are provided by (a) some clinopyroxene and plagioclases crystals with
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53 367 extremely variable age (≤ 6 ka to ≥ 23 ka; Kuritani *et al.*, 2020), (b) presence of zircons in the range
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55 368 1 ka-100 ka in trachytes (Zou *et al.*, 2021), and (c) dissolution textures which can not be explained

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3 369 by magma mixing (Yi *et al.*, 2021). According to available experimental data on alkaline magmas
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5 370 (Giuffrida *et al.*, 2017), the input of CO₂ in a magmatic system induces an enrichment in Ca of
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8 371 pyroxenes, a feature recorded in the microlites of the ME trachytes (Fig. 2B). The injection of deep
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10 372 CO₂ in the ME reservoir can destabilize the whole Changbaishan magmatic system and trigger ME.

11 12 373 13 14 15 374 *5.3 Rupture conditions of the ME reservoir*

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17 375 To estimate the rupture conditions of the ME reservoir, we set the top of the reservoir at about
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19 376 3.7 km depth (see above) and a density of the basement crustal rocks of 2700 kg/m³ (Choi *et al.*,
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21 377 2013); the resulting lithostatic pressure P_L is about 98 MPa. In the following, we assume that the fluid
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23
24 378 pressure P_f is the pressure exerted by CO₂ pushing the crust above the ME reservoir. We assume an
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26 379 extensional-shear rupture mechanism following the Griffith's criterion and determine P_f required to
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28 380 activate shear failure and crack opening at 3.7 km depth. The condition for an extensional-shear
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31 381 failure mode is given by (Sibson, 2000):

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34 382 \quad 4T \leq \sigma_1 - \sigma_3 \leq 5.66T(1)$$

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37 383 \quad P_f = \sigma_3 + [8T(\sigma_1 - \sigma_3) - (\sigma_1 - \sigma_3)^2] / 16T(2)$$

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40 384 where $\sigma_1 = P_L$ is the maximum stress, which is vertical in a normal stress regime, σ_3 is the horizontal
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42 385 least compressive stress and T is the tensile strength of the rocks. T varies between 14 and 8.5 MPa
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44 386 for intrusive and metamorphic rocks (Touloukian *et al.*, 1981) and we select an average value $T = 10$
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47 387 MPa. Using the above defined parameters, σ_3 is 49.7±8.3 MPa and $P_f = 58.8±9.2$ MPa. The obtained
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50 388 values are in the range of those required for the rupture of silicic chambers (10 to 100 MPa; Manga
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52 389 and Brodsky, 2006). We conclude that the pressure increase due to CO₂ entering the ME reservoir
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55 390 was enough to produce the failure the overlying crustal rocks. The fluid pressure increase estimated
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57 391 by us is larger than the minimum horizontal stress and roughly half of the lithostatic stress.

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3 392 5.4 The role of mantle fluids in triggering the 2002-2006 unrest at Changbaishan and the
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5 393 relationships between the recent dynamics and the ME reservoir
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8 394 The increase of CO₂, He and ³He/⁴He (R/Ra = 4.8 in 2002 and R/Ra = 6.6 in 2006) in the emitted
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10 395 gas during the 2002-2006 unrest episode at Changbaishan (Xu *et al.*, 2012) and the B isotopic values
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12 396 are compatible with fluids released from a deep, metasomatic mantle source (Zhao *et al.*, 2019). Such
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14 397 fluids may still enter the present-day ~ 4-8 km deep magmatic system. Otherwise, for example, the
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16 398 decay of U and Th in the magma chamber would result in continuously decreasing ³He/⁴He in the
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18 399 absence of the recharge of mantle-derived fluids or magmas (Moreira, 2013). This regional scale fluid
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20 400 release from the mantle is also supported by tomographic images (Lei *et al.*, 2013; Ma *et al.*, 2019),
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22 401 the huge CO₂ output in NE China including Changbaishan (2.1 Mt/yr), the ³He/⁴He values with R/Ra
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24 402 mostly between 3.5 and 6.5, and the ¹³C<sub>CO₂ values between -5.6 ‰ and -13.7 ‰ (Zhao *et al.*, 2021).
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26 403 At Changbaishan, a sudden decrease in the number of earthquakes between 2 and 7 km has been
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28 404 observed during the 2002-2006 unrest (Liu *et al.*, 2021) (Fig. 7). This depth range is characterized by
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30 405 significant variations in geophysical parameters and overlaps that inferred by us for the ME magma
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32 406 reservoir (Fig. 7). We propose that this reduction in the number earthquakes and, in the same depth
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34 407 range, of the values of density, resistivity, and S-wave velocities in the upper crust is due to melts
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36 408 possibly representing a residuum of the ME magma chamber. Therefore, the ME reservoir is, at least
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38 409 in part, active and, according to the gas and water geochemistry, is flushed by CO₂-rich fluids of deep
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40 410 origin released from a deeper basaltic reservoir located in the lower crust or at the mantle/crust
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42 411 interface, or from the sub-lithospheric metasomatized mantle (Ham *et al.*, 2008). In this framework,
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44 412 the 7 to 11 km deep earthquakes could indicate the input of such deep fluids (and melt?) in the nearly
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46 413 solid crystal-mush bottom of the reservoir, while the shallower earthquakes (≤ 2 km), which includes
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48 414 low-frequency events (Liu *et al.*, 2021), are related to the dynamics of the hydrothermal system likely
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50 415 destabilized from the transfer of such fluids from the reservoir to the shallower portions of the
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52 416 volcano. Accordingly, the earthquakes of the 2002-2006 unrest concentrated in the upper 2-3 km of
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3 417 the crust, where the hydrothermal system is stored (Zhang *et al.*, 2018), and just above the 2-6 km
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5 418 deep source of deformation modelled by levelling and GPS data (Xu *et al.*, 2012). This conceptual
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8 419 model of the ME magmatic system provides constraints on the interpretation of the causative factors
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10 420 of past and, possibly, future unrest episodes. Our study shows how regional scale deep, mantle fluids
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12 421 may alter the stability of crustal reservoirs responsible for large scale eruptions. In intraplate and rift
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14 422 settings characterized by the continuous release of the deep CO₂, the effects of a such gas upwelling
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17 423 on intra-crustal magmatic reservoirs could represents an underestimated cause of destabilization. The
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19 424 geodynamic, deep processes discussed here must be considered in the interpretation of monitoring
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21 425 signals to properly decipher the dynamics of large, active magmatic systems.
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25 427 **6. Conclusions**

26 428 The results of our analysis of the ME products may be summarized in the following points:

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28 429 1)The ME magmatic system consists in a single magma reservoir located at 3.7-7.5 km depth. This
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30 430 reservoir extends vertically for about 4 km and has a volume of 94 km³.
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33 431 2)The triggering mechanism of the ME eruption does not reflect processes internal to the reservoir
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35 432 but is related to the flushing of external carbon dioxide of deep, mantle origin. The arrival and
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37 433 progressive accumulation of deep carbon dioxide allowed the rupture of the ME reservoir. We
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39 434 exclude the arrival of a fresh and deeper trachytic magma into a rhyolitic magma reservoir or the
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41 435 increase of fluid pressure due to fractional crystallization processes alsone as triggering mechanism
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43 436 of the eruption.
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46 437 3)The fluid pressure induced by CO₂ flushing and required to destabilize the ME reservoir is in the
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48
49 438 order of 58.8±9.2 MPa at 3.7 km depth.
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51
52 439 4) The inferred depth of the ME reservoir is the same of that of some geophysical anomalies
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54 440 (resistivity, density, seismic wave velocities, hypocentral distribution of earthquakes of the 2002-
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56 441 2006 earthquakes). The 2002-2006 unrest reflects the destabilized of the residual reservoir of the ME
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3 442 by the arrival of CO₂-rich fluids from depth > 7-11 km and their transfer to the shallower (< 2-3 km
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5 443 depth) portions of the plumbing system of the volcano.

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8 444 Our results highlight the role of regional scale processes as the upraising of mantle-derived fluids
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10 445 in NE China in the destabilization of shallow magma chambers associated to large scale eruptions.
11
12 446 Geodynamic processes should be taken into account when interpreting unrest episodes at volcanoes.
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30 455 Academy of Sciences, Natural Science Foundation of China.

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676 **Figure captions**

677 **Figure 1.** Geodynamic setting of Changbaishan volcano and 'Millenium' eruption stratigraphy. **(A)**
678 Location of the Changbaishan volcano, depth of the earthquakes of the Pacific slab (white dashed
679 lines; from Zhang *et al.*, 2018) and dispersion of 'Millenium' eruption rhyolitic fall deposit (isopaches
680 in dashed yellow lines redrawn from Horn and Schmincke, 2000). **(B)** Simplified W-E tomography

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3 681 profile (from Ma *et al.*, 2019) extending from China to Japan and crossing the Changbaishan volcano.
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5 682 The main petrogenetic processes and their depth are summarized according to Xu *et al.* and Zhang *et*
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7 683 *al.*, 2015, 2018). (C) Topography of the Changbaishan volcano and dispersion of the ME pyroclastic
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9 684 flow deposits (from Pan *et al.*, 2017). Numbers indicate the sampling localities (samples are listed in
10 685 the Supplementary Information). (D) Representative outcrop and rocks of the ME eruption fall
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12 686 deposit (sampling locality 2 in Fig. 1C).

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14 687
15 688 **Figure 2.** Chemical features of ME rocks. (A) TAS (Total Alkali vs. Silica) diagram. Glass (matrix-
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17 689 glass): new data from this study, literature data from Pan *et al.*; melts inclusion (MI): data from
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19 690 Iacovino *et al.* (2016) (B) Composition of pyroxene phenocrysts and microlites from literature data.

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22 692 **Figure 3.** Volatile content in ME rocks. (A) Silica vs. Cl, (B) silica vs. F and (C) silica vs. H₂O
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24 693 (EMPA data). (D) Normalized histograms for H₂O (TGA data). (E) Normalized histograms for CO₂
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26 694 and (F) normalized histograms for S (CSA data) in glasses. Data from this study and Pan *et al.* (2017)
27 695 and melts inclusions (MI; data from Iacovino *et al.* 2016) in D,E,F are normalized to allow
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29 696 comparison between the different samples.

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32 698 **Figure 4.** 3D images of ME rocks acquired through X-ray microtomography. Three-dimensional
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34 699 renderings of representative (A) white pumice, (B) dark scoriae and (C) banded scoria of ME.
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36 700 Diameter of cylinder is 5000 μm . The vesicles are black, the matrix-glass is dark-gray, minerals are
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38 701 light gray or white. Note the sinuous banding with deformed bubbles in the white pumice and the
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40 702 large vesicles attached to crystals in the dark scoria.

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43 704 **Figure 5.** 3D textural features of ME rocks. (A) Vesicle volume distributions. (B) Cumulative
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45 705 vesicle size distributions. (C) Normalized histogram of vesicles size. (D) Vesicle size vs. ratio
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47 706 between the longest and shortest Feret diameter for representative samples. WP: white pumices (solid
48 707 and long dashed green lines), DS: dark scoriae (solid red lines), BC: banded clasts (short dashed
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50 708 lines). For the sample K1-banded no chemical analyses are available.

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53 710 **Figure 6.** Magmatic processes recorded by H₂O vs. CO₂ contents. (A) H₂O vs. CO₂ concentration
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55 711 in glasses (this study) and melt inclusions (data from Iacovino *et al.* 2016) for the ME rhyolitic rocks.
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57 712 (B) H₂O vs. CO₂ concentration in glasses (this study) and melt inclusions (data from Iacovino *et al.*,
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59 713 2016) for the ME trachytic rocks. Saturation curves for rhyolite and trachyte at 800 °C were calculated
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3 714 according to Liu *et al.* (2005) and Papale *et al.* (2006). The inset in (A) shows the processes that
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5 715 typically control different H₂O-CO₂ trends.
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8 717 **Figure 7.** Seismicity of the 2002-2006 time period and interpretative model of the unrest. Epicentral
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10 718 distribution of the earthquakes during the 2002-2006 unrest (data from Liu *et al.*, 2021), number of
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12 719 earthquakes with depth and time evolution of the seismicity. The depth of the magma reservoir of
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14 720 ME estimated in this study is reported as a vertical red bar. The main geophysical anomalies from
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16 721 previous studies are reported as vertical blue bars (Choi *et al.*, 2013; Qiu *et al.*, 2014; Hammond *et*
17 722 *al.*, 2020). The arrows indicate the different processes involved during the unrest and discussed in the
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19 723 text.
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22 725 **Supplementary Items**

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24 726 **Table S1. List of samples.** Rock samples collected from the different sampling sites (shown in Fig.
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26 727 1C).

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28 728 **Table S2. Geochemical data for White-Pumice.** Major elements, Cl and F concentrations in matrix-
29
30 729 glass through Electron Micro Probe Analyzer (EMPA).

31 730 **Table S3. Geochemical data for Dark-Scoria.** Major elements, Cl and F concentrations in matrix-
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33 731 glass through Electron Micro Probe Analyzer (EMPA)

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35 732 **Table S4. Geochemical data for Gray-Green-Scoria.** Major elements, Cl and F concentrations in
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37 733 matrix-glass through Electron Micro Probe Analyzer (EMPA).

38 734 **Table S5. Geochemical data for K1-White.** Major elements, Cl and F concentrations in matrix-
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40 735 glass through Electron Micro Probe Analyzer (EMPA).

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42 736 **Table S6. Volatile content in matrix-glasses.** H₂O data through thermogravimetric (TGA),
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44 737 CO₂ and S through Carbon/Sulfur Analyses (CSA).

45 738 **Table S7. 3D textural data.** Analyses performed using X-ray computed microtomography.

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47 739 **Figure. S1. 3D image of White-Pumice (caldera rim).** 3D volume rendering and 2D orthogonal
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49 740 slices obtained through X-ray computed microtomography.

50 741 **Figure. S2. 3D image of Dark-Scoria (caldera rim).** 3D volume rendering and 2D orthogonal
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52 742 slices obtained through X-ray computed microtomography.

53 743 **Figure. S3. 3D image of Gray-Green-Scoria (caldera rim).** 3D volume rendering and 2D
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55 744 orthogonal slices obtained through X-ray computed microtomography.

56 745 **Figure. S4. 3D image of Sample3-White (caldera rim).** 3D volume rendering and 2D orthogonal
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58 746 slices obtained through X-ray computed microtomography.
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3 747 **Figure. S5. 3D image of Sample3-Dark (caldera rim).** 3D volume rendering and 2D orthogonal
4 slices obtained through X-ray computed microtomography.

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6 749 **Figure. S6. 3D image of K1-Banded (caldera rim).** 3D volume rendering and 2D orthogonal slices
7 obtained through X-ray computed microtomography.

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10 751 **Figure. S7. 3D image of Sample1-White (intermediate-distal area).** 3D volume rendering and 2D
11 orthogonal slices obtained through X-ray computed microtomography.

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13 753 **Figure. S8. 3D image of CPF5 (intermediate-distal area).** 3D volume rendering and 2D orthogonal
14 slices obtained through X-ray computed microtomography.

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17 755 **Figure. S9. 3D image of Western-Plain (intermediate-distal area).** 3D volume rendering and 2D
18 orthogonal slices obtained through X-ray computed microtomography.

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20 757 **Figure. S10. 2D image of K1-White.** 2D (backscattered electron) images obtained through Scanning
21 Electron Microscope (SEM).

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24 759 **Figure. S11. 2D image of K1-Dark.** 2D (backscattered electron) images obtained through Scanning
25 Electron Microscope (SEM).

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27 761 **Figure. S12. 2D image of Sample3-Dark.** 2D (backscattered electron) images obtained through
28 Scanning Electron Microscope (SEM).

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31 Scanning Electron Microscope (SEM).

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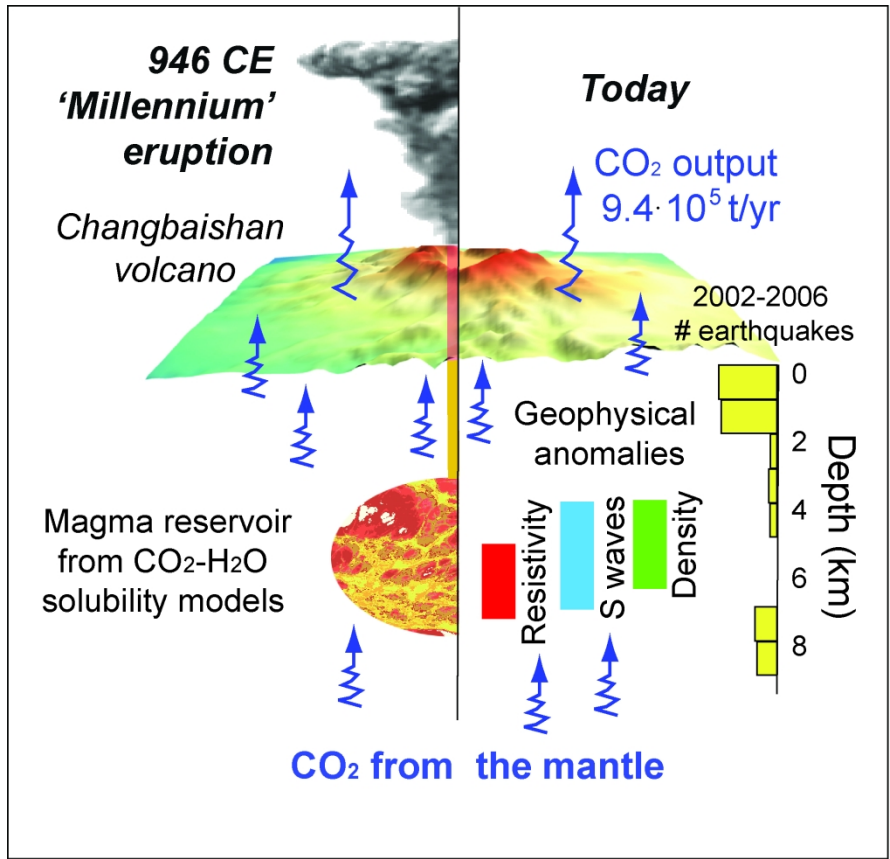
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Highlights

- The Millennium eruption magmatic system of Changbaishan volcano consists in a single magma reservoir located at 3.7-7.5 km depth
- The triggering mechanism of the ME eruption is related to the flushing of external carbon dioxide of deep, mantle origin
- The 2002-2006 unrest reflects the destabilized of the residual reservoir of the ME by the arrival of CO₂-rich fluids
- The upraising of mantle-derived fluids in NE China may have played an important role in the destabilization of shallow magma chambers and associated large scale eruptions

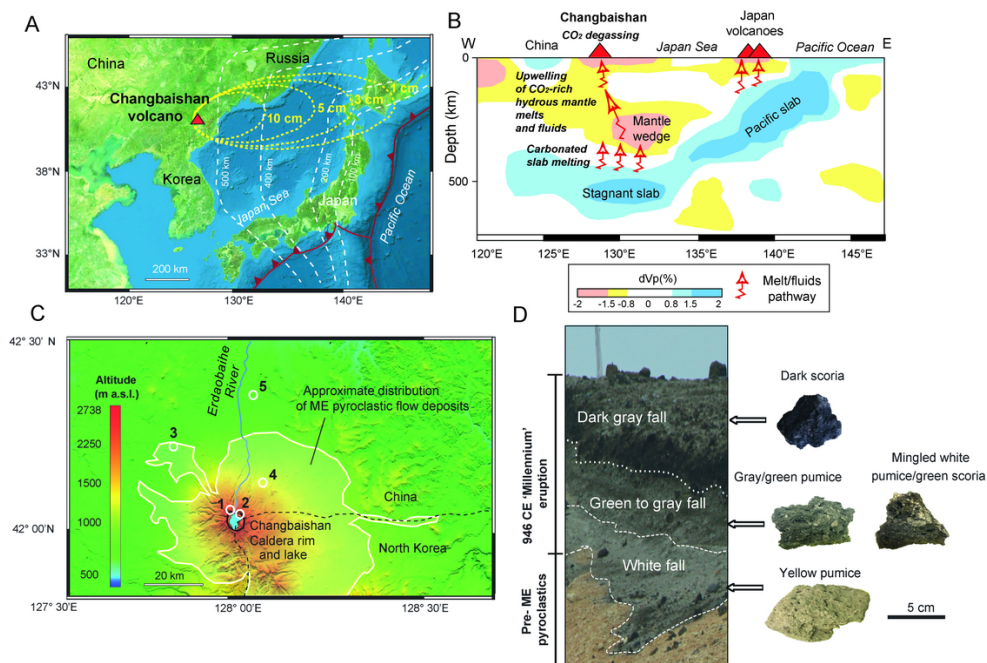


Figure 1. Geodynamic setting of Changbaishan volcano and 'Millenium' eruption stratigraphy. (A) Location of the Changbaishan volcano, depth of the earthquakes of the Pacific slab (white dashed lines; from Zhang et al., 2018) and dispersion of 'Millenium' eruption rhyolitic fall deposit (isopaches in dashed yellow lines redrawn from Horn and Schmincke, 2000). (B) Simplified W-E tomography profile (from Ma et al., 2019) extending from China to Japan and crossing the Changbaishan volcano. The main petrogenetic processes and their depth are summarized according to Xu et al. and Zhang et al., 2015, 2018). (C) Topography of the Changbaishan Caldera rim and lake and dispersion of the ME pyroclastic flow deposits (from Pan et al., 2017). Numbers indicate the sampling localities (samples are listed in the Supplementary Information). (D) Representative outcrop and rocks of the ME eruption fall deposit (sampling locality 2 in Fig. 1C).

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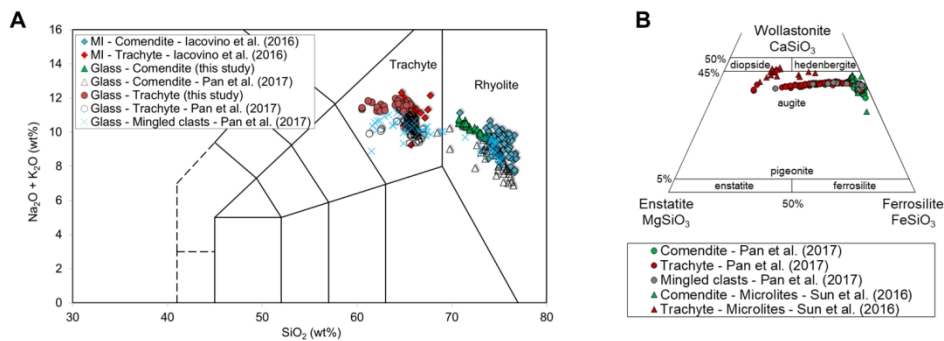


Figure 2. Chemical features of ME rocks. (A) TAS (Total Alkali vs. Silica) diagram. Glass (matrix-glass): new data from this study, literature data from Pan et al.; melts inclusion (MI): data from Iacovino et al., (2016) (B) Composition of pyroxene phenocrysts and microlites from literature data.

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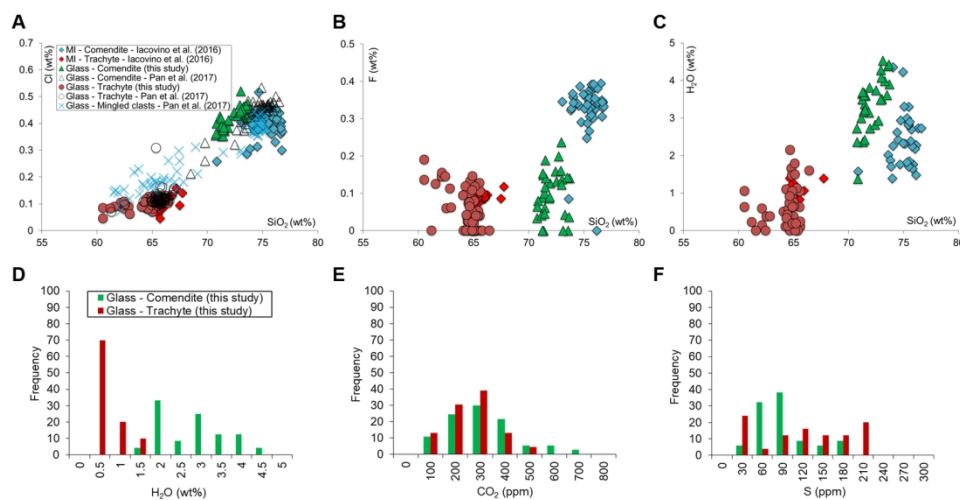


Figure 3. Volatile content in ME rocks. (A) Silica vs. Cl, (B) silica vs. F and (C) silica vs. H₂O (EMPA data). (D) Normalized histograms for H₂O (TGA data). (E) Normalized histograms for CO₂ and (F) normalized histograms for S (CSA data) in glasses. Data from this study and Pan et al. (2017) and melts inclusions (MI; data from Iacovino et al., 2016) in D,E,F are normalized to allow comparison between the different samples.

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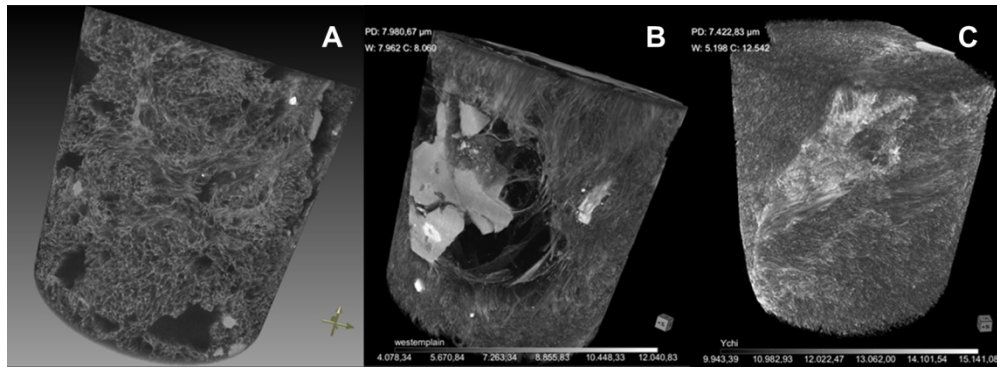


Figure 4. 3D images of ME rocks acquired through X-ray microtomography. Three-dimensional renderings of representative (A) white pumice, (B) dark scoriae and (C) banded scoria of ME. Diameter of cylinder is 5000 μm . The vesicles are black, the matrix-glass is dark-gray, minerals are light gray or white. Note the sinuous banding with deformed bubbles in the white pumice and the large vesicles attached to crystals in the dark scoria.

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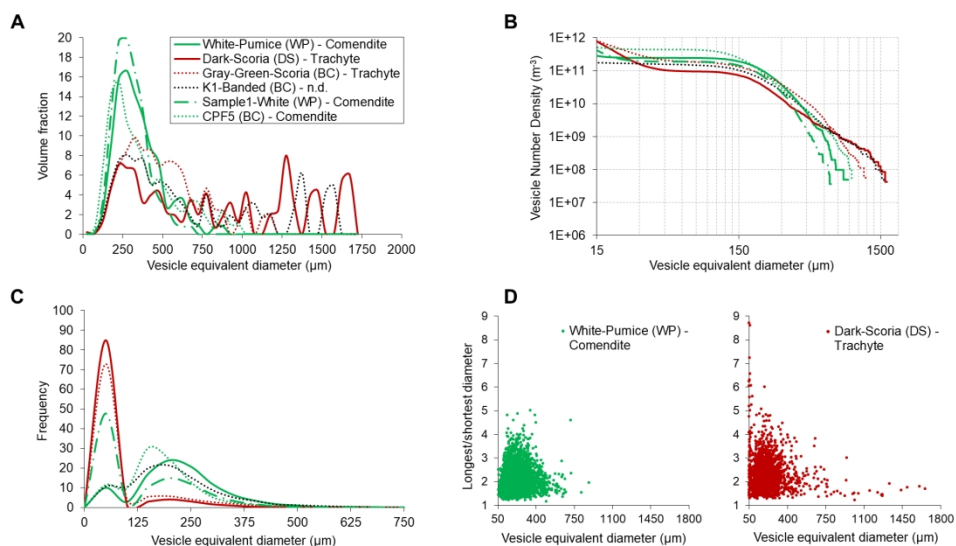


Figure 5. 3D textural features of ME rocks. (A) Vesicle volume distributions. (B) Cumulative vesicle size distributions. (C) Normalized histogram of vesicles size. (D) Vesicle size vs. ratio between the longest and shortest Feret diameter for representative samples. WP: white pumices (solid and long dashed green lines), DS: dark scoriae (solid red lines), BC: banded clasts (short dashed lines). For the sample K1-banded no chemical analyses are available.

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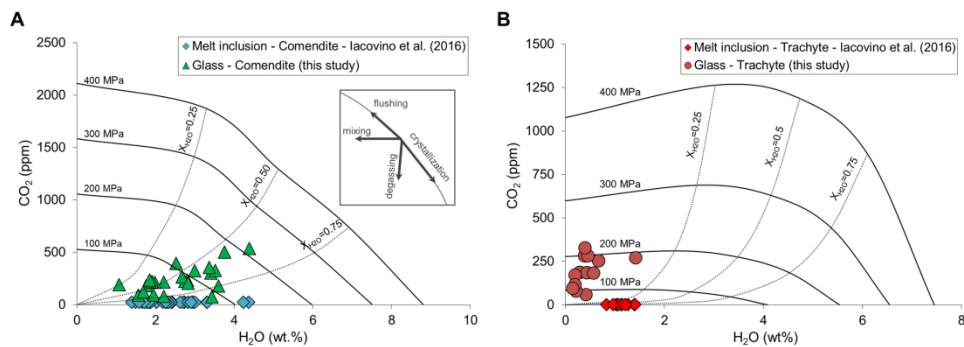


Figure 6. Magmatic processes recorded by H₂O vs. CO₂ contents. (A) H₂O vs. CO₂ concentration in glasses (this study) and melt inclusions (data from Iacovino et al., 2016) for the ME rhyolitic rocks. (B) H₂O vs. CO₂ concentration in glasses (this study) and melt inclusions (data from Iacovino et al., 2016) for the ME trachytic rocks. Saturation curves for rhyolite and trachyte at 800 °C were calculated according to Liu et al. (2005) and Papale et al. (2006). The inset in (A) shows the processes that typically control different H₂O-CO₂ trends.

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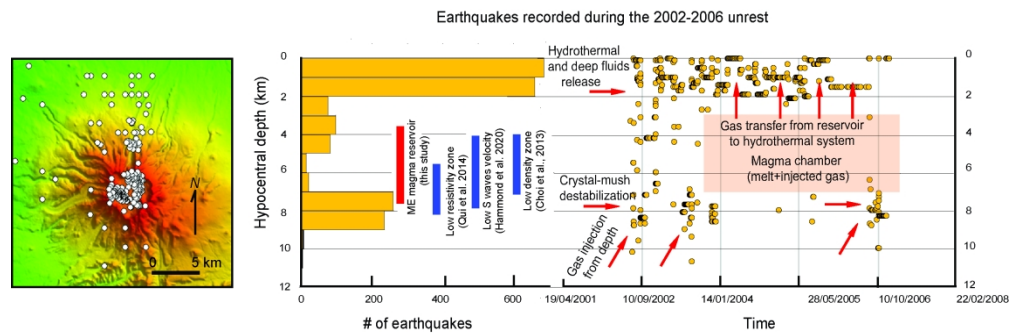


Figure 7. Seismicity of the 2002-2006 time period and interpretative model of the unrest. Epicentral distribution of the earthquakes during the 2002-2006 unrest (data from Liu et al., 2021), number of earthquakes with depth and time evolution of the seismicity. The depth of the magma reservoir of ME estimated in this study is reported as a vertical red bar. The main geophysical anomalies from previous studies are reported as vertical blue bars (Choi et al., 2013; Qiu et al., 2014; Hammond et al., 2020). The arrows indicate the different processes involved during the unrest and discussed in the text.

Table S1. List of samples. Rock samples collected from the different sampling sites (shown in Fig. 1C).

Sampling site	Samples	Type of deposit	Correspondent in Yi et al. (2021) to:
1	K1-Yellow, K1-Dark, K1-Banded	Fallout	Section 2-3, Sample U3-U5
2	Sample3-Yellow, Sample3-Dark, Sample3-Banded, Yellow-Pumice, Dark-Scoria, Gray-Green-Scoria	Fallout	Section 1 (Tianwen Section), Sample U3-U5
3	Western-Plain	Fallout	-
4	CFP5	Fallout	-
5	Sample1-Yellow	PDCs	-

GPS coordinates (Lat. - Long.) of the sampling sites:

- 1- 42° 1'55.58"N - 128° 3'18.80"E
 2- 42° 1'32.61"N - 128° 4'9.28"E
 3- 42° 5'31.26"N - 127°47'34.17"E
 4- 42°12'23.54"N - 128°13'5.91"E
 5- 42°23'12.62"N - 128° 5'48.73"E

Table S2. Geochemical data for Yellow-Pumice. Major elements, Cl and F concentrations in matrix-glass through Electron Micro Probe Analyzer (EMPA).

SiO₂	68.62	68.82	69.86	69.60	69.01	69.62	69.99	69.05	69.09	68.74
TiO₂	0.20	0.33	0.43	0.32	0.31	0.33	0.21	0.20	0.31	0.31
Al₂O₃	11.65	11.59	11.73	11.05	11.52	11.44	10.87	11.22	11.40	11.36
FeO	4.82	5.16	5.03	5.02	4.95	4.95	5.16	4.87	5.10	4.97
MnO	0.06	0.12	0.04	0.11	0.11	0.10	0.07	0.08	0.11	0.08
MgO	0.07	0.10	0.10	0.08	0.12	0.11	0.15	0.09	0.03	0.13
CaO	0.31	0.36	0.33	0.20	0.34	0.39	0.30	0.37	0.15	0.40
Na₂O	5.77	6.03	6.13	5.45	5.75	5.87	5.52	5.92	5.63	5.49
K₂O	4.30	4.21	4.43	4.56	4.43	4.29	4.43	4.30	4.62	4.52
P₂O₅	0.08	0.09	0.00	0.00	0.00	0.05	0.00	0.05	0.00	0.00
Cl	0.36	0.35	0.39	0.37	0.41	0.34	0.40	0.37	0.39	0.40
F	0.09	0.03	0.08	0.08	0.04	0.15	0.12	0.06	0.00	0.00
SO₃	0.01	0.08	0.07	0.00	0.01	0.00	0.05	0.05	0.01	0.09
total	96.34	97.27	98.62	96.84	97.00	97.64	97.27	96.63	96.84	96.49
SiO₂	68.80	69.16	68.97	69.74	69.11	68.85				
TiO₂	0.15	0.18	0.27	0.27	0.27	0.17				
Al₂O₃	11.30	11.01	11.42	11.34	11.93	11.50				
FeO	4.73	5.15	4.91	5.03	4.83	4.82				
MnO	0.14	0.13	0.09	0.09	0.06	0.12				
MgO	0.11	0.06	0.05	0.12	0.05	0.02				
CaO	0.34	0.26	0.23	0.31	0.40	0.35				
Na₂O	5.92	5.40	5.58	5.73	6.04	5.71				
K₂O	4.39	4.35	4.38	4.41	4.49	4.43				
P₂O₅	0.00	0.00	0.00	0.02	0.00	0.00				
Cl	0.34	0.40	0.36	0.37	0.35	0.36				
F	0.10	0.09	0.14	0.11	0.06	0.04				
SO₃	0.02	0.00	0.01	0.04	0.04	0.02				
total	96.34	96.19	96.41	97.58	97.63	96.39				

Table S3. Geochemical data for Dark-Scoria. Major elements, Cl and F concentrations in matrix-glass through Electron Micro Probe Analyzer (EMPA).

SiO ₂	64.89	65.54	62.04	65.29	64.46	59.91	64.89	60.16	63.73	63.30
TiO ₂	0.42	0.36	1.05	0.40	0.44	1.27	0.56	0.93	0.42	0.45
Al ₂ O ₃	15.75	15.89	16.51	15.50	15.87	17.29	16.05	17.16	15.83	15.72
FeO	4.81	4.73	5.22	5.03	4.94	4.89	4.75	5.69	4.91	4.77
MnO	0.12	0.14	0.11	0.07	0.15	0.11	0.10	0.15	0.14	0.06
MgO	0.34	0.18	0.76	0.27	0.26	0.89	0.33	1.01	0.29	0.36
CaO	1.14	1.33	2.26	1.27	1.27	2.46	1.37	2.38	1.33	1.40
Na ₂ O	5.76	5.86	5.77	6.05	5.95	6.13	6.03	5.98	5.71	5.78
K ₂ O	5.50	5.49	5.46	5.60	5.64	5.11	5.78	5.36	5.73	5.60
P ₂ O ₅	0.09	0.14	0.37	0.12	0.19	0.52	0.19	0.37	0.00	0.11
Cl	0.10	0.12	0.09	0.10	0.12	0.08	0.10	0.05	0.09	0.12
F	0.04	0.11	0.14	0.05	0.01	0.19	0.10	0.14	0.13	0.13
SO ₃	0.01		0.07	0.02		0.08	0.07		0.03	0.04
total	98.97	99.89	99.85	99.77	99.30	98.93	100.32	99.38	98.34	97.84
SiO ₂	64.57	65.52	64.78	65.46	65.36	63.96	63.77	65.15	64.21	62.30
TiO ₂	0.33	0.51	0.52	0.45	0.57	0.48	0.56	0.65	0.54	0.84
Al ₂ O ₃	15.79	15.89	16.01	15.87	15.82	15.36	16.33	15.58	16.53	17.42
FeO	4.89	4.71	4.83	4.66	4.78	4.83	4.89	4.93	4.66	4.19
MnO	0.14	0.02	0.15	0.10	0.10	0.11	0.15	0.15	0.10	0.09
MgO	0.28	0.32	0.27	0.20	0.22	0.30	0.30	0.24	0.34	0.68
CaO	1.32	1.08	1.24	1.30	1.29	1.25	1.39	1.25	1.42	1.90
Na ₂ O	5.93	6.01	6.00	6.01	6.02	6.06	6.04	5.75	5.86	5.71
K ₂ O	5.49	5.85	5.52	5.56	5.75	5.46	5.86	5.39	5.84	5.87
P ₂ O ₅	0.00	0.09	0.14	0.06	0.22	0.19	0.06	0.00	0.16	0.43
Cl	0.10	0.09	0.11	0.10	0.11	0.11	0.09	0.13	0.10	0.08
F	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.13	0.12	0.06
SO ₃	0.03	0.07	0.07	0.00	0.08	0.10	0.06	0.02	0.02	0.06
total	98.87	100.20	99.64	99.77	100.32	98.21	99.50	99.37	99.90	99.63
SiO ₂	61.78	61.71	62.63	61.07	62.51					
TiO ₂	0.82	1.09	0.85	1.15	0.81					
Al ₂ O ₃	17.07	17.60	17.20	17.83	17.34					
FeO	4.85	4.55	4.54	4.41	4.59					
MnO	0.09	0.05	0.15	0.05	0.08					
MgO	0.60	0.73	0.61	0.68	0.64					
CaO	1.96	2.07	1.71	2.10	2.17					
Na ₂ O	5.64	5.89	5.61	5.94	5.86					
K ₂ O	5.74	5.87	5.85	5.86	5.36					
P ₂ O ₅	0.53	0.40	0.20	0.56	0.36					
Cl	0.10	0.09	0.09	0.08	0.11					
F	0.15	0.13	0.11	0.00	0.15					
SO ₃	0.08	0.02	0.08	0.04	0.11					
total	99.41	100.20	99.63	99.77	100.09					

Table S4. Geochemical data for Gray-Green-Scoria. Major elements, Cl and F concentrations in matrix-glass through Electron Micro Probe Analyzer (EMPA).

10	SiO₂	64.17	64.19	65.35	63.89	63.04	64.30	64.60	64.39	64.77	63.63
11	TiO₂	0.64	0.58	0.45	0.48	0.84	0.48	0.59	0.56	0.56	0.53
12	Al₂O₃	16.49	16.52	16.19	16.18	16.94	16.28	16.09	16.62	16.32	16.37
13	FeO	4.64	4.85	5.18	4.77	5.09	4.54	4.77	4.94	4.60	4.58
14	MnO	0.04	0.09	0.11	0.09	0.06	0.10	0.15	0.09	0.09	0.06
15	MgO	0.36	0.36	0.25	0.28	0.64	0.28	0.35	0.32	0.41	0.43
16	CaO	1.42	1.39	1.23	1.19	1.80	1.34	1.32	1.29	1.34	1.48
17	Na₂O	5.74	5.52	5.77	5.43	5.62	5.75	6.16	5.81	5.88	5.81
18	K₂O	5.53	5.81	5.68	6.08	5.66	5.74	5.81	5.61	5.54	5.86
19	P₂O₅	0.17	0.11	0.19	0.02	0.22	0.14	0.12	0.06	0.11	0.02
20	Cl	0.10	0.09	0.11	0.08	0.06	0.10	0.08	0.12	0.11	0.10
21	F	0.07	0.04	0.08	0.00	0.06	0.00	0.00	0.02	0.05	0.00
22	SO₃	0.04	0.04	0.08	0.04	0.07	0.05	0.07	0.05	0.02	0.04
23	total	99.41	99.59	100.67	98.53	100.10	99.10	100.11	99.88	99.80	98.91
24	SiO₂	64.55	64.22	64.71	64.66	64.17	65.87	64.14	64.91	64.05	64.20
25	TiO₂	0.54	0.50	0.61	0.53	0.53	0.57	0.48	0.62	0.42	0.63
26	Al₂O₃	16.26	16.22	16.42	16.19	15.95	15.83	16.53	16.32	16.39	16.84
27	FeO	4.60	4.82	4.78	4.77	4.74	4.72	4.54	4.82	4.54	4.71
28	MnO	0.16	0.11	0.10	0.10	0.09	0.09	0.13	0.07	0.12	0.15
29	MgO	0.32	0.29	0.41	0.29	0.34	0.27	0.38	0.37	0.38	0.37
30	CaO	1.29	1.25	1.39	1.31	1.33	1.42	1.34	1.39	1.29	1.39
31	Na₂O	5.67	5.75	5.95	5.73	5.81	5.55	5.72	5.75	5.90	5.95
32	K₂O	5.71	5.57	5.66	5.49	5.28	5.48	5.62	5.50	5.63	5.66
33	P₂O₅	0.00	0.00	0.00	0.06	0.00	0.13	0.20	0.00	0.13	0.09
34	Cl	0.07	0.12	0.10	0.08	0.10	0.11	0.08	0.12	0.08	0.09
35	F	0.02	0.00	0.02	0.08	0.12	0.00	0.08	0.11	0.06	0.09
36	SO₃	0.06	0.10	0.06	0.06	0.05	0.04	0.01	0.05	0.09	0.06
37	total	99.25	98.95	100.21	99.35	98.51	100.08	99.25	100.03	99.08	100.23
38	SiO₂	64.51	65.38	64.16	64.80	65.11					
39	TiO₂	0.62	0.47	0.70	0.48	0.50					
40	Al₂O₃	16.07	16.08	16.39	16.22	15.93					
41	FeO	4.84	4.77	4.75	4.89	4.73					
42	MnO	0.15	0.10	0.09	0.12	0.13					
43	MgO	0.29	0.32	0.39	0.34	0.30					
44	CaO	1.22	1.23	1.36	1.39	1.27					
45	Na₂O	5.92	4.13	6.05	5.53	5.72					
46	K₂O	5.50	5.73	5.56	5.66	5.82					
47	P₂O₅	0.09	0.06	0.06	0.06	0.09					
48	Cl	0.11	0.10	0.11	0.11	0.11					
49	F	0.02	0.00	0.04	0.15	0.04					
50	SO₃	0.02	0.03	0.01	0.06	0.05					
51	total	99.36	98.40	99.67	99.81	99.80					

Table S5. Geochemical data for K1-Yellow. Major elements, Cl and F concentrations in matrix-glass through Electron Micro Probe Analyzer (EMPA).

SiO₂	69.79	70.82	70.34	70.37	70.36	70.40	70.46	69.82	70.84	70.58
TiO₂	0.36	0.21	0.30	0.30	0.28	0.29	0.33	0.29	0.17	0.25
Al₂O₃	10.35	9.58	9.76	10.63	10.14	9.72	9.78	9.87	9.94	10.28
FeO	4.95	5.08	4.98	4.86	4.99	5.06	5.41	5.16	5.09	5.00
MnO	0.05	0.07	0.12	0.06	0.08	0.03	0.11	0.11	0.12	0.08
MgO	0.08	0.07	0.04	0.09	0.06	0.04	0.09	0.06	0.04	0.06
CaO	0.30	0.14	0.19	0.21	0.22	0.27	0.17	0.21	0.27	0.31
Na₂O	5.48	5.36	4.92	5.73	5.29	5.22	5.37	5.26	5.32	5.63
K₂O	4.23	4.05	4.43	4.24	4.09	4.00	4.14	4.27	4.00	4.24
P₂O₅	0.06	0.09	0.08	0.00	0.00	0.05	0.00	0.00	0.02	0.00
Cl	0.41	0.44	0.40	0.43	0.45	0.45	0.50	0.45	0.45	0.42
F	0.13	0.14	0.00	0.15	0.04	0.03	0.13	0.23	0.14	0.19
SO₃	0.06	0.04	0.06	0.10	0.01	0.01	0.00	0.00	0.00	0.02
total	96.25	96.09	95.62	97.17	96.01	95.57	96.49	95.73	96.4	97.06

SiO₂	69.79	70.37	68.65	70.00	69.19
TiO₂	0.29	0.35	0.29	0.27	0.30
Al₂O₃	10.11	9.91	11.30	10.10	11.25
FeO	4.85	5.08	4.92	5.05	4.74
MnO	0.10	0.13	0.10	0.04	0.07
MgO	0.11	0.13	0.15	0.08	0.07
CaO	0.25	0.33	0.29	0.27	0.31
Na₂O	5.39	5.33	5.72	5.36	5.77
K₂O	4.12	4.28	4.37	4.18	4.40
P₂O₅	0.00	0.00	0.00	0.00	0.05
Cl	0.43	0.42	0.38	0.43	0.37
F	0.00	0.16	0.15	0.12	0.18
SO₃	0.02	0.02	0.00	0.03	0.08
total	95.46	96.51	96.32	95.93	96.78

Table S6. Volatile content in matrix-glasses. H₂O data through thermogravimetric (TGA), CO₂ and S through Carbon/Sulfur Analyses (CSA).

Sample	H ₂ O (wt%)	CO ₂ (ppm)	S (ppm)	Sample	H ₂ O (wt%)	CO ₂ (ppm)	S (ppm)	
Yellow - Pumice	2.81	230.10	12.78	K1-White	3.43	72.50	77.80	
		323.50	60.40			151.60	60.35	
	3.75	499.10	87.99			1.56	89.10	69.94
		618.20	65.83				106.50	64.37
	2.67	262.00	119.07			2.82	203.30	50.06
	2.99	323.80	48.23				138.40	58.29
		339.90	36.59			4.38	534.80	78.44
Dark-Scoria	0.67	252.30	85.08			448.70	91.08	
		303.10	95.74			219.10	80.27	
	0.54		98.33	K1-Dark	0.44	184.50	30.00	
	0.40	326.50	19.27			0.39	281.50	20.63
		438.30	82.98			1.42	269.92	14.59
	372.50	86.82			0.15	94.53	1.64	
						171.28	21.32	
Gray-Green-Scoria	0.42	58.30	138.50	Sample1-White	2.52	392.80	34.65	
			133.95				544.30	78.86
	0.57	181.70	156.82			1.88	219.70	57.09
		263.20	123.23			1.76	180.20	51.57
	0.20	169.80	99.24			1.91	218.70	61.58
	0.46	280.80	103.87		CPF5	2.74	222.00	138.71
	220.20	46.69				247.60	165.42	
Sample3-Yellow	3.40	300.40	73.67			1.95	90.70	157.78
		333.10	91.42			2.21	79.10	154.26
	3.51	326.70	24.95			1.07	191.00	148.23
	3.60	176.60	30.39	Western-Plain	2.21	214.50		
	3.36	355.80	51.12			1.98	213.10	62.53
Sample3-Dark	0.29	185.40	195.08			1.69	120.20	
		278.30	173.10				107.30	
		158.40	166.65			1.85	233.30	47.99
		277.90	182.64			123.50	57.74	
	0.22	79.60	182.30					
		206.90	192.01					
	0.20	115.90	181.90					

Table S7. 3D textural data. Analyses performed using X-ray computed microtomography.

Sample	Yellow - Pumice	Dark- Scoria	Gray-Green- Scoria	K1- Banded	Sample1- Yellow	CPF5
Total volume (mm³)	63.59	63.60	63.51	63.51	63.52	63.55
Vesicle volume (mm³)	45.21	40.63	46.40	43.32	37.27	46.49
Melt volume (mm³)	18.38	22.96	17.11	20.20	26.26	17.06
Number of vesicles (diameter > 15 μm)	5572	15717	13187	3576	10067	9330
Mean vesicle size (μm)	198	50	75	189	117	157
Porosity (%)	71	64	73	68	59	73
Vesicle interconnection	99.98	99.58	99.67	91.00	99.88	99.98
VND_{bulk} (Vesicle Number density; m³)	8.76E-08	2.47E-07	2.08E-07	5.63E-08	1.58E-07	1.47E-07
VND_{melt} (Vesicle Number density; m³)	3.03E+11	6.84E+11	7.71E+11	1.77E+11	3.83E+11	5.47E+11

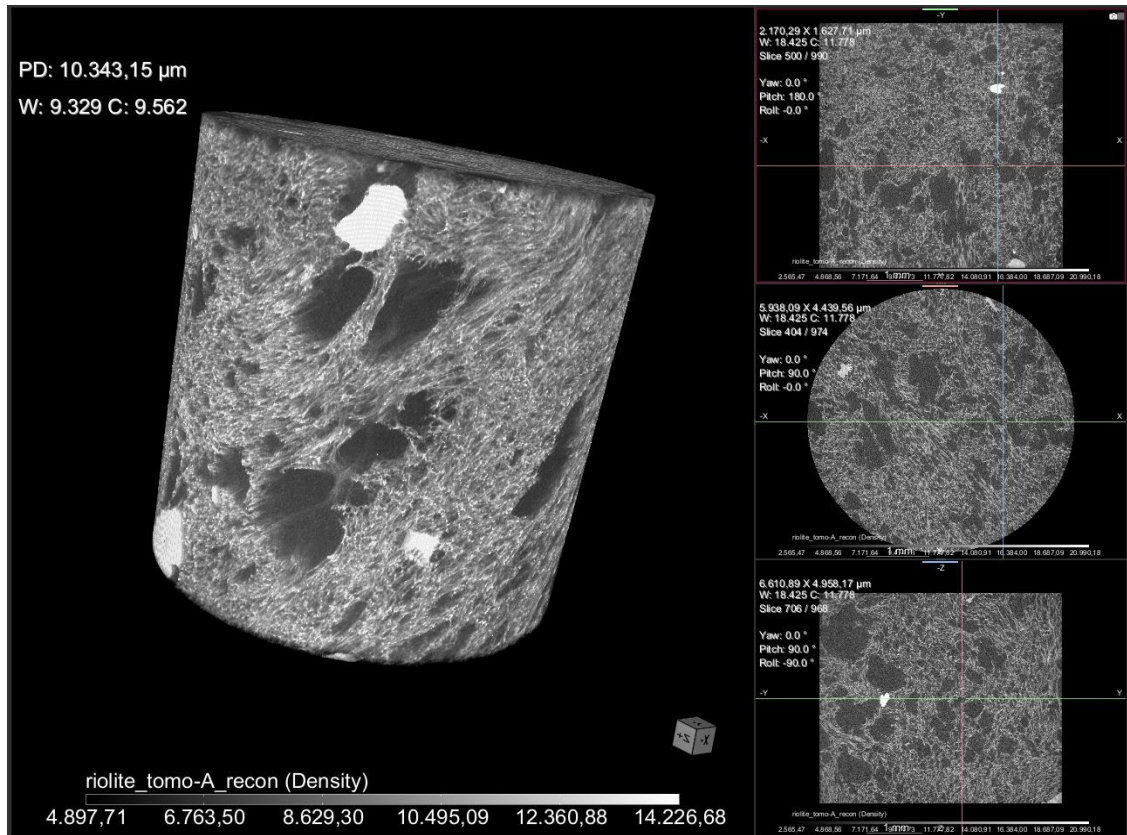


Fig. S1. 3D image of Yellow -Pumice (Tianwen site, site 2 in Fig. 1C). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

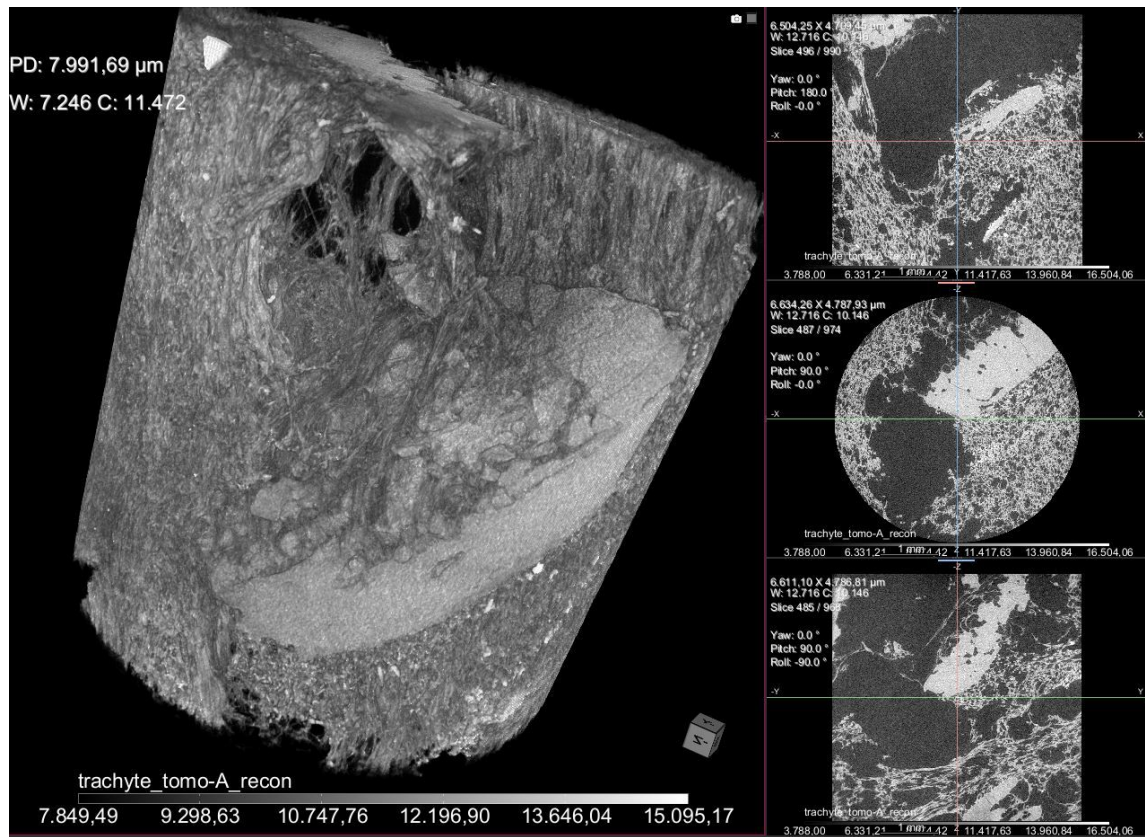


Fig. S2. 3D image of Dark-Scoria (Tianwen site, site 2 in Fig. 1C). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

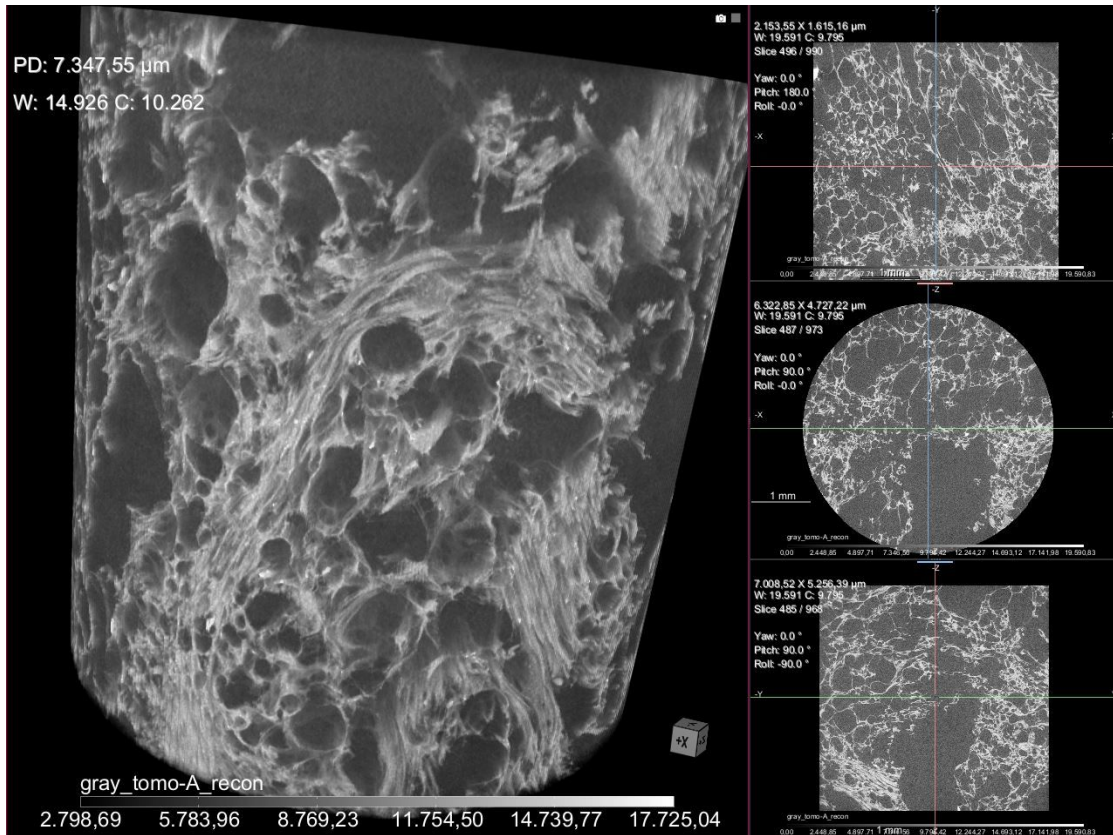


Fig. S3. 3D image of Gray-Green-Scoria (Tianwen site, site 2 in Fig. 1C). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

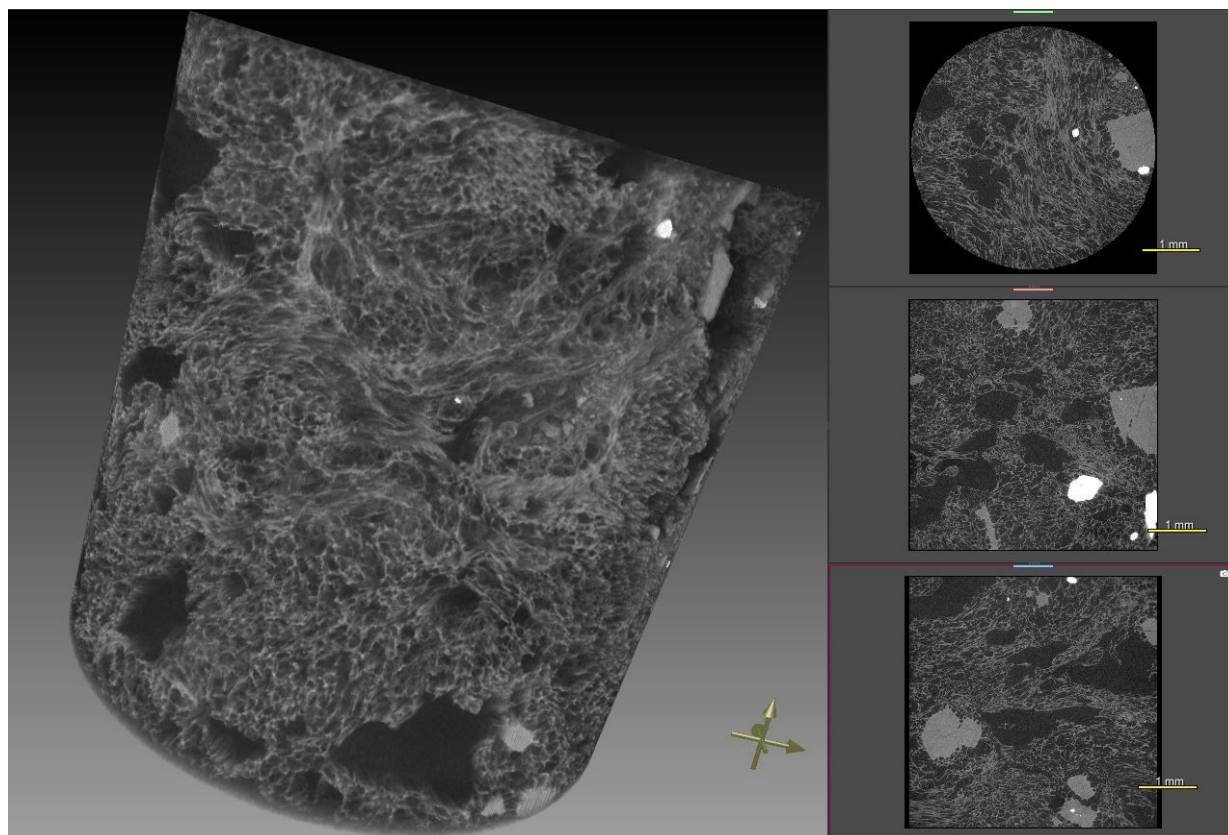


Fig. S4. 3D image of Sample3- Yellow (Tianwen site, site 2 in Fig. 1C). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

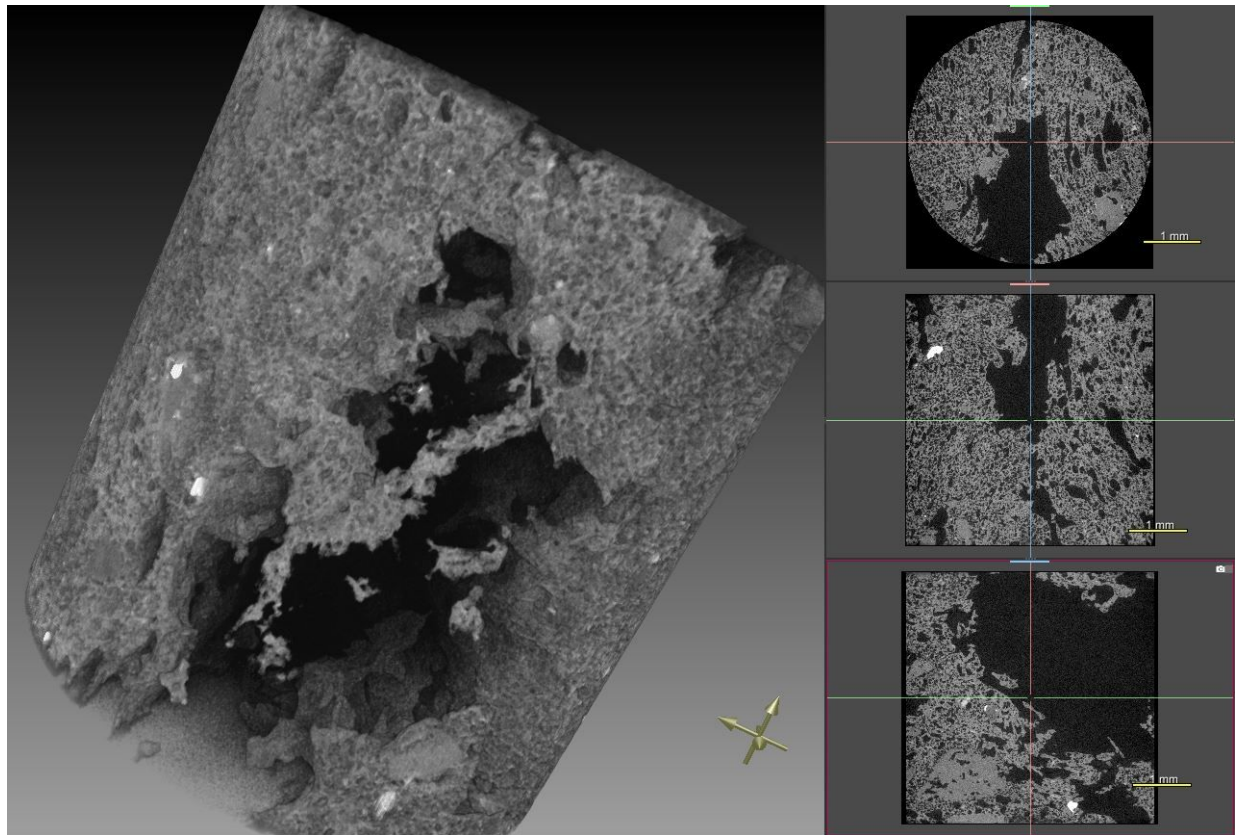


Fig. S5. 3D image of Sample3-Dark (Tianwen site, site 2 in Fig. 1C). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

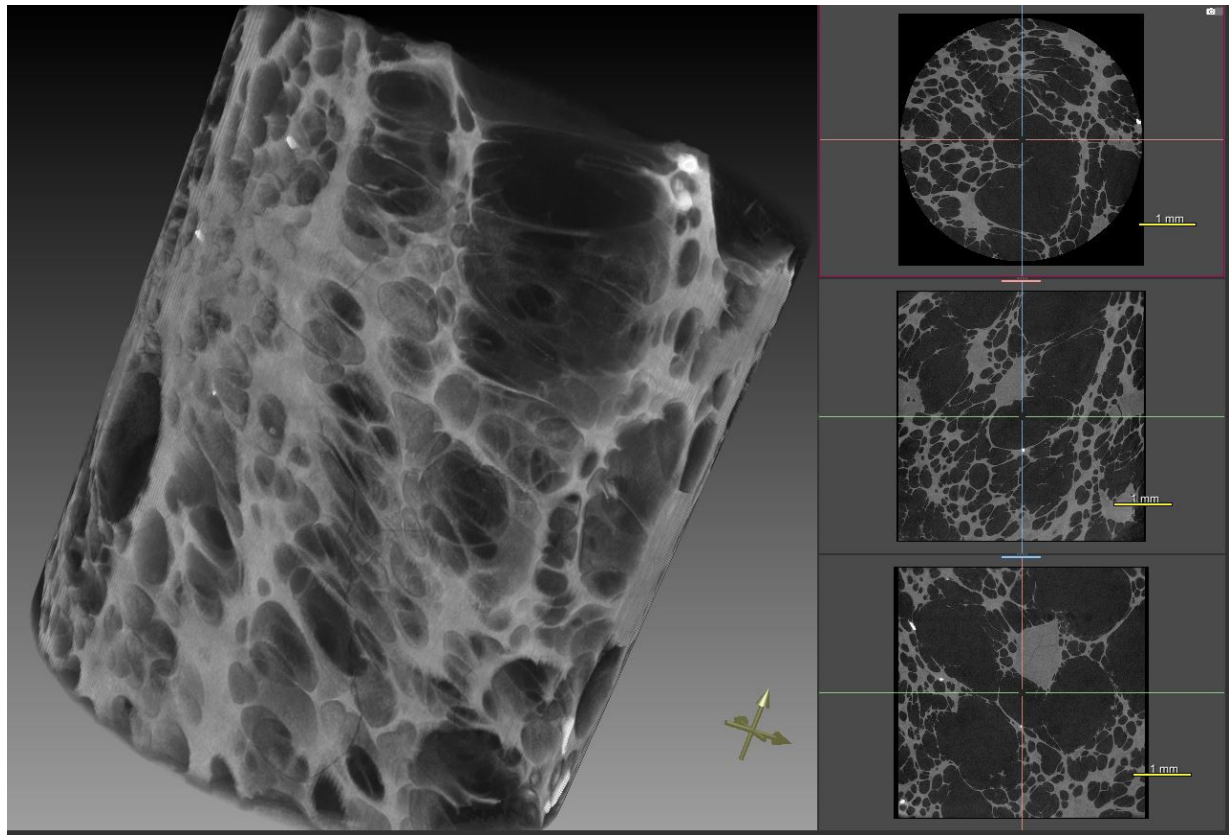


Fig. S6. 3D image of K1-Banded (Tianwen site, site 2 in Fig. 1C). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

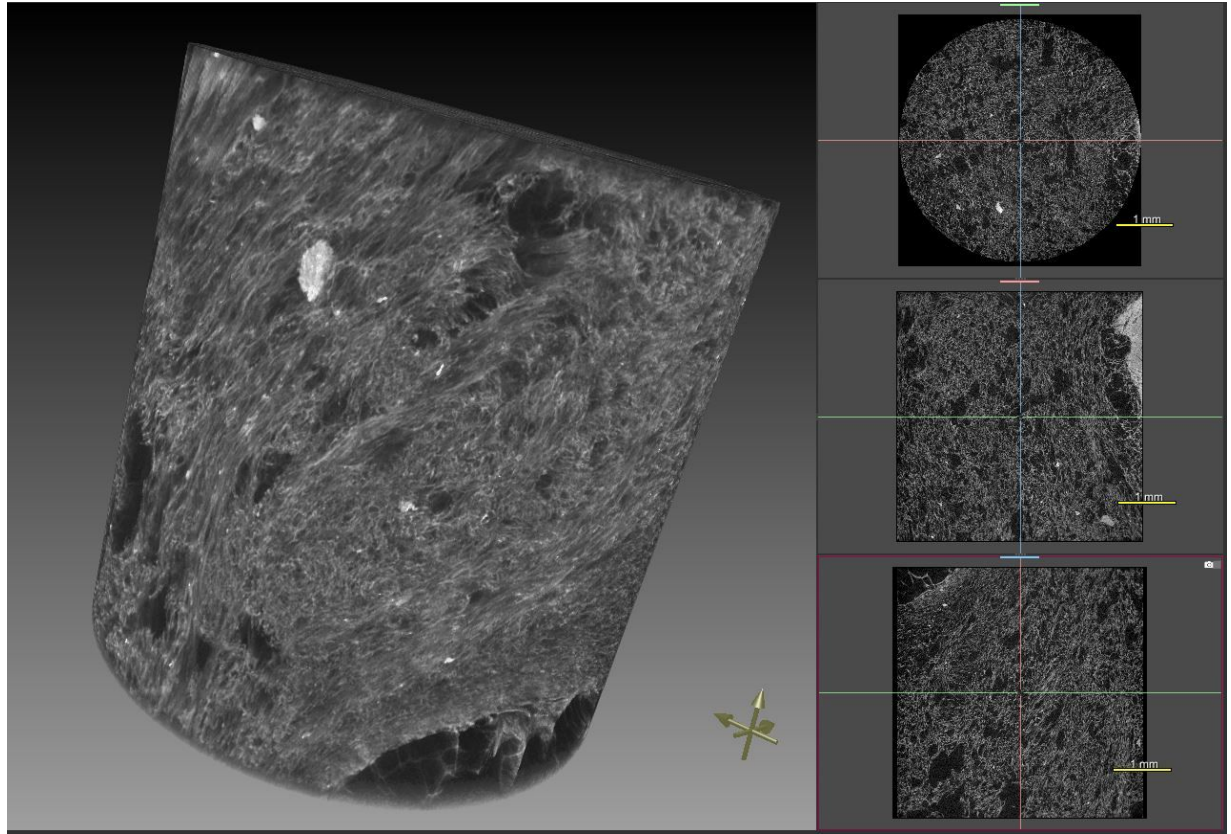


Fig. S7. 3D image of Sample1-Yellow (intermediate-distal area). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

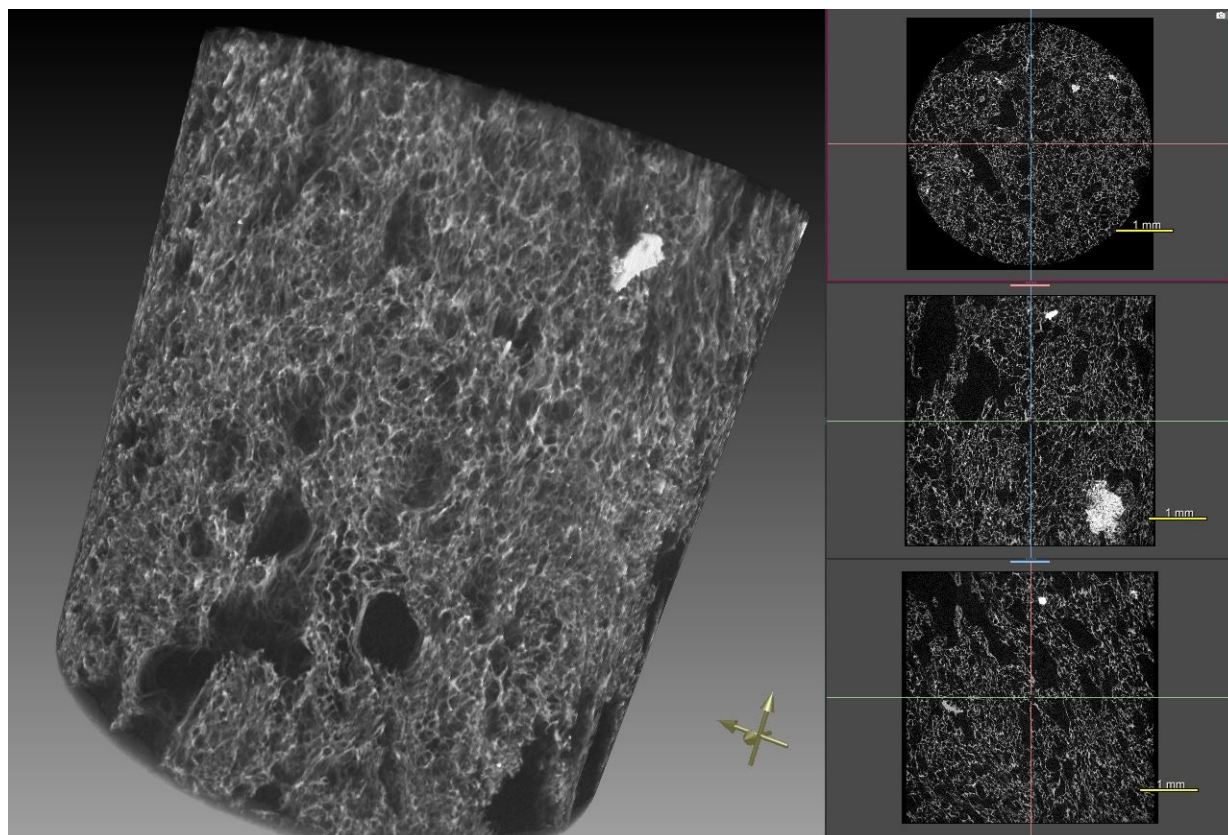


Fig. S8. 3D image of CPF5 (intermediate-distal area). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

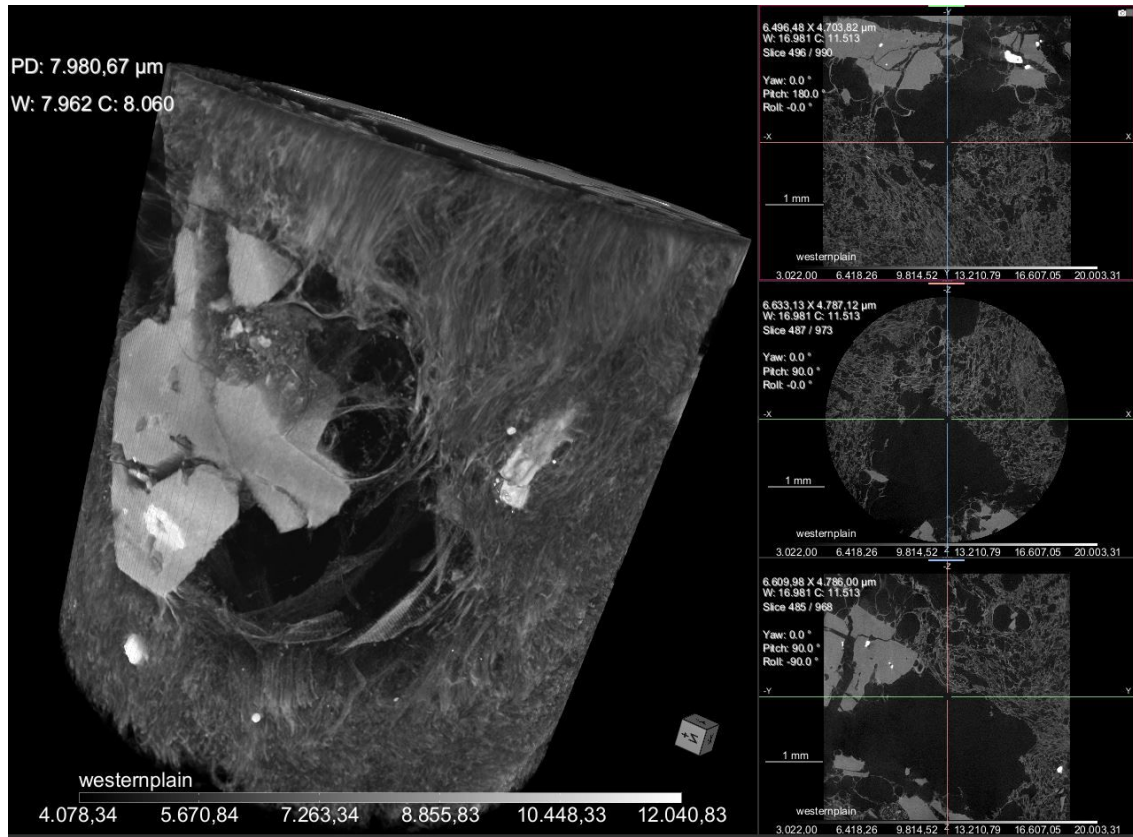


Fig. S9. 3D image of Western-Plain (intermediate-distal area). 3D volume rendering and 2D orthogonal slices obtained through X-ray computed microtomography.

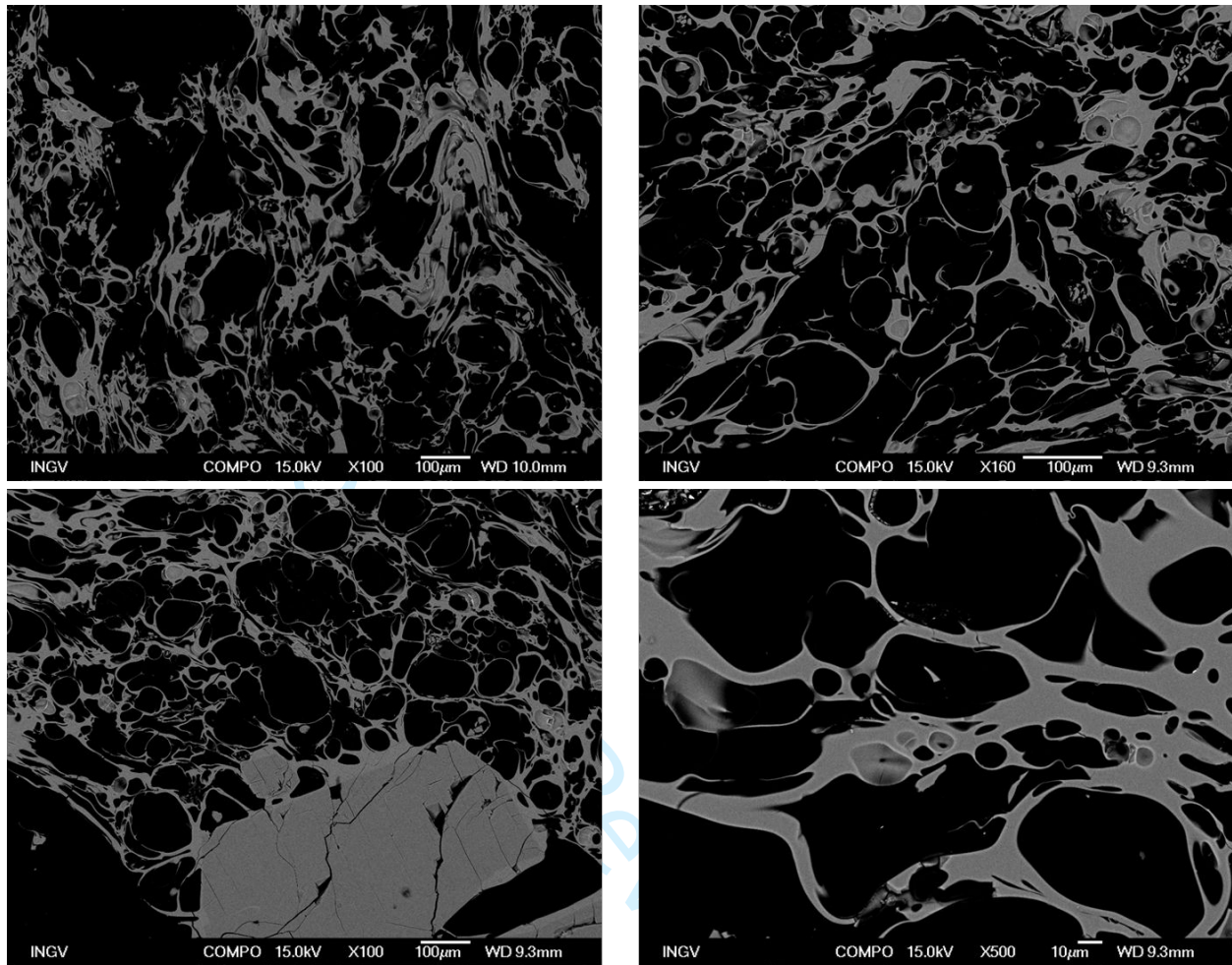


Fig. S10. 2D image of K1-Yellow. 2D (backscattered electron) images obtained through Scanning Electron Microscope (SEM).

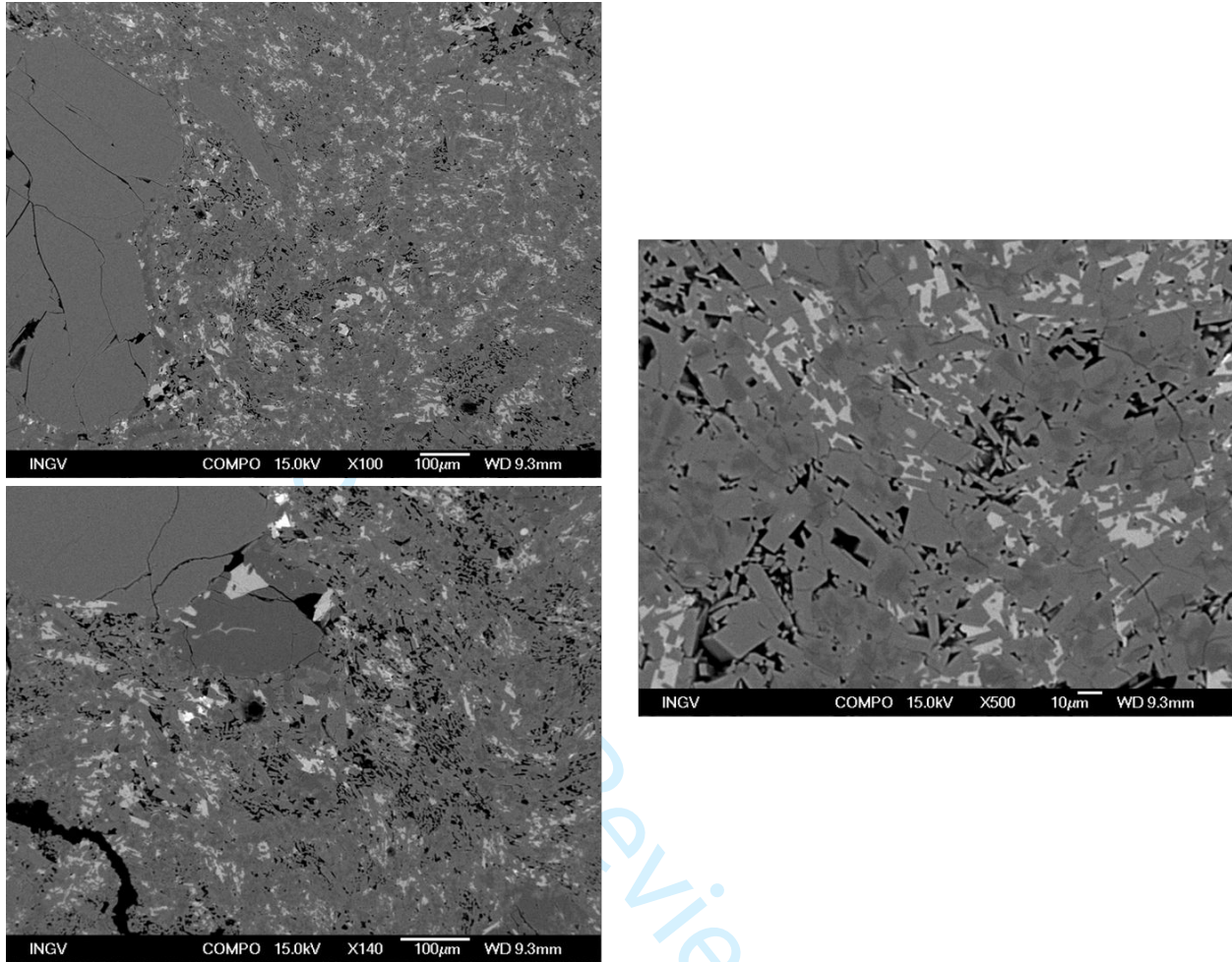


Fig. S11. 2D image of K1-Dark. 2D (backscattered electron) images obtained through Scanning Electron Microscope (SEM).

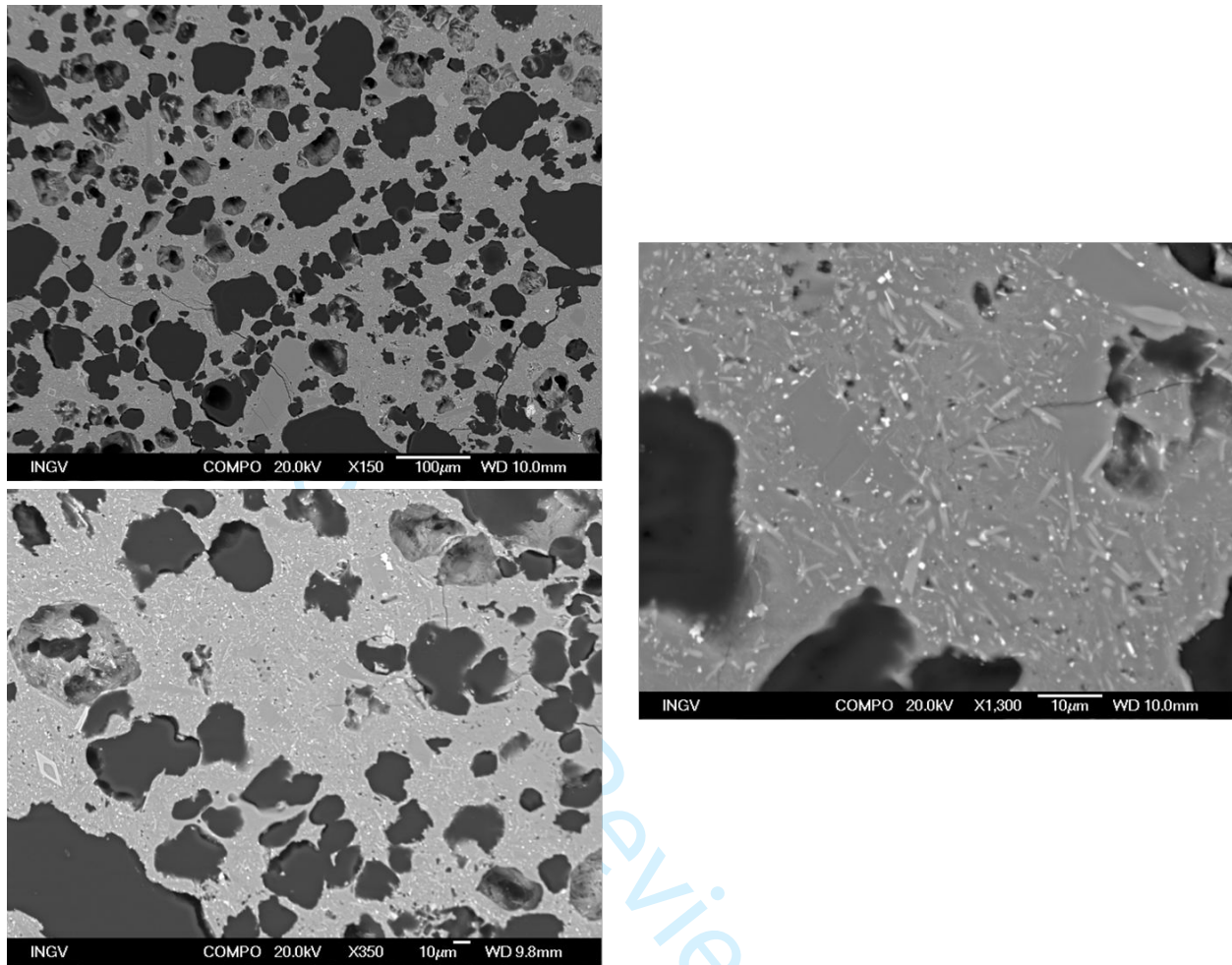


Fig. S12. 2D image of Sample3-Dark. 2D (backscattered electron) images obtained through Scanning Electron Microscope (SEM).

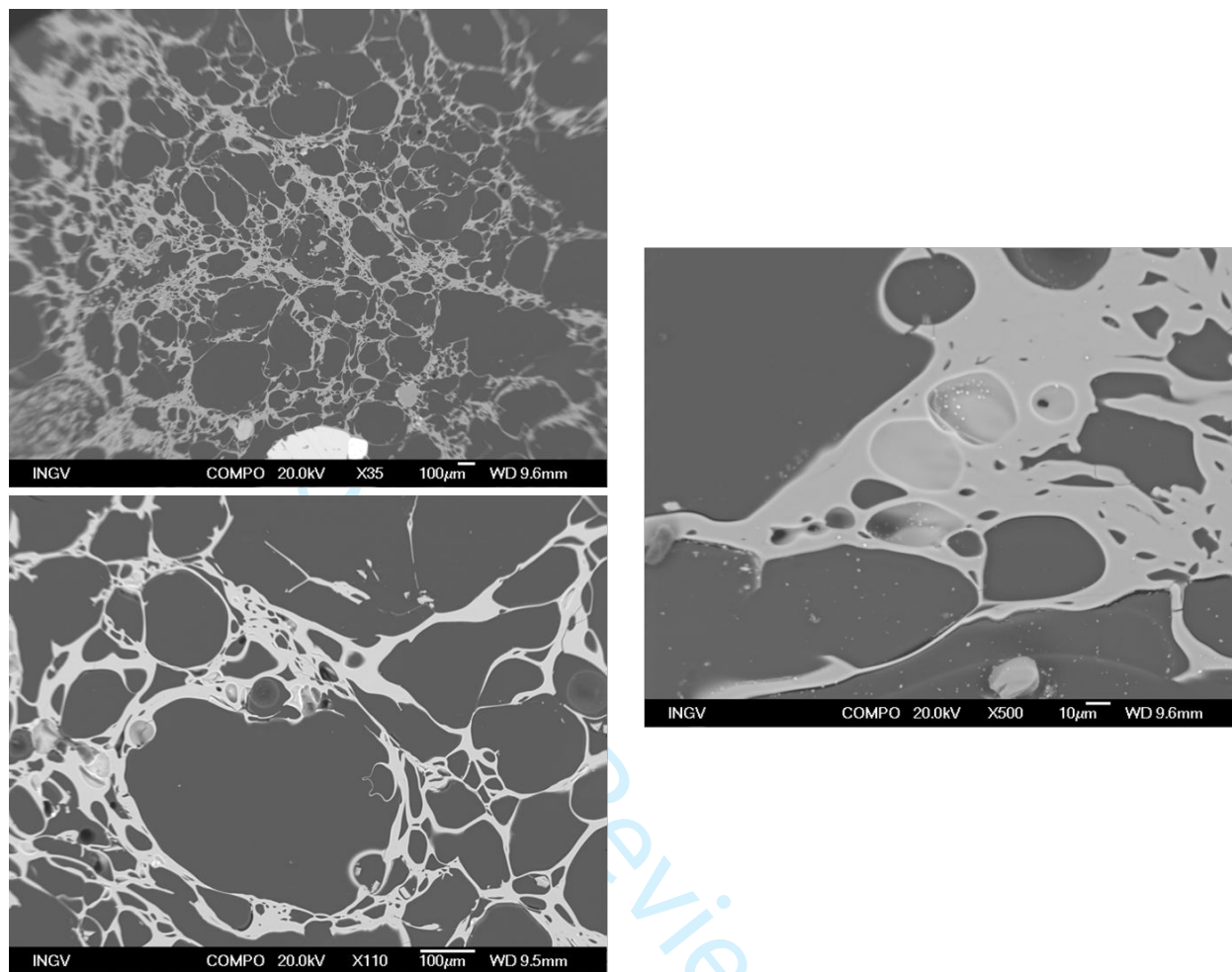


Fig. S13. 2D image of Gray-Green-Scoria. 2D (backscattered electron) images obtained through Scanning Electron Microscope (SEM).