Subducted iron and glassy spherules in the upper mantle?

¿Esférulas de hierro y vítreas subducidas en el manto superior?

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ABSTRACT

Spherules are documented in ophiolitic mantle rocks such as peridotites and associated chromitites. They consist of: (1) native iron having variable amounts of Ni with/without inclusions of silicate glass or oxides (wüstite), (2) dendritic intergrowth of oxides (magnetite, wüstite and hematite) with/without silicate glass and, (3) silicate glass. Consensually, they are interpreted as indigenous to chromitites and related with high-temperature processes operating in the Earth's upper mantle. However, their similarity with terrestrial and extraterrestrial spherules found in other settings of the geological record is remarkable. We raise the question on such indigenous origin, relating them to volcanic and cosmic material recycled back to the mantle wedge where chromitites form during subduction.

Keywords: spherules, iron, glass, upper mantle, chromitite, subduction.

RESUMEN

Rocas del manto superior ofiolitico tales como peridotitas y cromititas contienen esferas. Estas consisten de: (1) hierro native con cantidades variables de Ni con y sin inclusiones de vidrio silicatdo y óxidos (wüstite), (2) intercrecimientos dendríticos de óxidos (magnetita, wüstita y hematites) con o sin vidrio silicatado y, (2) vidrio silicatado. Unísonamente, estas esférulas se interpretan como indígenas a las cromititas y relacionadas con procesos de alta temperatura que tienen lugar en el manto superior terrestre. Sin embargo, su parecido con aquellas esferas de origen terrestre y extraterrestre descritas en otros contextos geológicos es reseñable. En este trabajo cuestionamos el origen autóctono de las esferas en las rocas mantélicas, interpretándolas como material de origen volcánico y cósmico que ha sido reciclado atraves de la cuña de manto superior donde ser forman las cromititas durante los procesos de subducción.

Palabras clave: esferas, metal, vidrio, manto superior, cromitita, subducción.

INTRODUCTION

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1. Introduction

Millimetric to (sub)-microscopic metallic-silicate-oxide spherules of both extraterrestrial and terrestrial origins are present in the fossil and current geological record. The extraterrestrial ones are part of the huge number of micrometeorites and cosmic dust that rains on the Earth annually resulting from the fragmentation of asteroids and released from comets (Peucker-Ehrenbrink, 2001). Such extraterrestrial material enters the atmosphere and partially melts and oxidizes to form tiny (<2 mm) spheroidal bodies consisting of iron or iron-nickel oxides and/or alloys (I-type), Fe oxide dendrites within silicate glass (G-type) or mainly silicate (S-type; with the V subtype made up only of silicate glass) (Genge *et al.*, 2008). On Earth, metallic-silicate-glass spherules may form by: (1) high-temperature processes but related with volcanism (i.e., cloud-to-ground lightning strikes or eruptions of low-viscosity magmas; Genaerau *et al.*, 2015; Nyström *et al.*, 2016), (2) meteoritic impact (i.e., crystallization from the splash ejecta or condensation from rock-vapor plumes; Velázquez *et al.*, 2021), (3) biogenic hydrothermal activity (Agarwal *et al.*, 2021), and (3) diagenesis (Suk *et al.*, 1990). Likewise, un-natural anthropogenetic industrial processes may also manufacture spherules (Niyogi *et al.*, 2011; McCloy, 2019).

Metallic-oxide-silicate spherules are also found in mantle rocks (peridotites and chromitites) from a few ophiolites (Bai *et al.*, 2004; Robinson *et al.*, 2004; Xu *et al.*, 2009; Xu *et al.*, 2015; Yang *et al.* 2015; Griffin *et al.*, 2016), although its origin is highly controversial. They are interpreted to from within mantle itself by melt immiscibility under the highly reducing conditions (e.g., Griffin *et al.*, 2016; Xiong *et al.*, 2017) or to be solid products of molten droplets originated by lightning strikes on the mantle rocks when exposed to Earth's surface (Ballhaus *et al.*, 2017). Here we provide the first-ever thoughtful comparative study of metallic-oxide-silicate spherules from ophiolitic upper mantle rocks with others present in the geological record, raising the possibility that they could correspond to recycled airborne spherules of cosmic

and volcanic origin that originally landed on the deep-sea floor were recycled back to the mantle during subduction. Our discovery offers an innovative alternative to foster the current debate of exotic minerals in ophiolitic rocks while unravelling geodynamic processes that operate in subduction-zone settings.

2. Analytical methods

2.1. MINERAL CONCENTRATES

A small chip from each of the four samples analyzed in this study (GK1C-1 and GK3A-1 from Golyamo Kamenyane and J-410m and Y-409m from Yakovitsa) was pre-grounded in agate mortar, washed with ethanol and then dried at room temperature for few minutes (until complete evaporation of the ethanol). Dry material was then divided into sub fractions by handheld magnet, pre-insulated from direct contact with the material to avoid contamination, and purified several times. In order to avoid potential contamination, the manipulations of washing with ethanol were done in glass Petri dish and the acid treatment in PTFE containers (100 ml tanks). This way, two fractions were separated – non-magnetic, silicate one, and magnetic chromite one. As a precaution, the material was inspected under a binocular microscope at each step of the separation process and no spherules were detected at this stage. Each fraction was subsequently separated by granulometry using 200 mesh disposable sieves while the fraction 70-100 μm was again checked for spherules, although they were not identified. The chromite fractions were further treated with a mixture of HF and HCl acid, heated to 160° C. The insoluble residue was then washed with deionized water several times and dried at room temperature revealing the presence of spherules when recognized under binocular microscope. Once recognized, the spherules were hand-picked and sticked on a wire of carbon tape on a SEM pin stub holder to be imaged under scanning electron microscopy. Subsequent to this preliminary analysis of the

spherule surface, then they were imbibed in epoxy resin and polished. Considering the small size and their softness, the largest iron spherule identified from the Yakovitsa chromitite was the only to survive the polishing process.

2.2. FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FE-SEM)

Spherules were preliminarily characterized and imaged using a Leo Gemini Field Emission Scanning Electron Microscope (FE-SEM) at the Centro de Instrumentación Científica (CIC) of the Universidad de Granada, Spain. The instrument was equipped with an Energy Dispersive Spectra (EDS) detector. Accelerating voltage was 20 kV and beam current optimized for an adequate number of counts for each EDS analysis. The unpolished spherules were firstly inspected on the secondary electron mode (SE) in an effort to better define their morphological characteristics and chemistry by EDX, where once polished they were checked again under FESEM but using the back-scattered electron mode (BSE), although only one of the spherules survived (i.e., Spherule 1 from Yakovitsa shown in Figure 2 of the main text).

2.3. MICRO-RAMAN

The micro-Raman spectra of silicate and oxide component of the spherules were obtained by means of JASCO NRS-5100 micro-Raman spectrometer, equipped with an Olympus microscope with x5, x20, and x100 objectives belonging to the CIC of University of Granada, Spain. The 532 nm laser excitation was used as an excitation source with a spectral resolution of 2.08 cm^{-1}. The minimum lateral resolution was about 1 µm (with the 100× objective). The spectrometer was calibrated using the 520.6 cm-1 Raman peak of silicon before each experimental measurement. The spectra were collected using the 100× objective with repeated acquisition: 2 acquisitions for 100 s. Obtained Raman spectra were compared with those of the RRUFF database.

2.4. ELECTRON MICROPROBE ANALYSIS (EPMA)

The major element composition of magnetite was determined on the polished surface for the Spherule 1 using a Cameca SX-100 microprobe in CIC of University of Grana, Spain.

EPMA data were obtained using an excitation voltage of 20 kVand a beamcurrent of 20 nA, with a beam 2–3 µm in diameter. Monitored spectral lines were MgKα, FeKa, AlKα, CrKα, SiKα, TiKα, MnKα, NiKα, CoKα, ZnKα and VKα. Standards used were MgO, Fe$_2$O3, Al$_2$O$_3$, Cr$_2$O$_3$, SiO$_2$, CoO, ZnO, TiO$_2$, MnTiO$_3$, NiO and Pb$_5$(VO$_4$)$_3$Cl.

2.5. FOCUSED ION BEAM (FIB) HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM)

A thin-foil sample was prepared and extracted from the polished Spherule-1 from the Yakovitsa chromitite by using a Focused Ion Beam Scanning Electron Microscope (FIB-SEM) in the Laboratorio de Microscopías Avanzadas (LMA) at the Instituto de Nanociencia de Aragón (INA) – University of Zaragoza, Spain. The TEM thin foil preparation was performed using a Dual Beam FEI Thermo-Fisher Scientific, model Helios 650. The selected region of interest was first covered by a thin strip (~300 nm) of C by focused electron beam induced deposition (FEBID) and subsequently with a second strip (~1 µm) of Pt. These strips act as protection during the milling, polishing, and extraction process of the thin foils. The bulk material was first removed on both sides of the lamella by a rough Ga$^+$ ion milling with a 30 kV current at 2.5 nA and the subsequent polishing with a 30 kV current at 0.23 nA. The final polishing step was performed on the sample's inclusions until the electron transparency was achieved. This was completed by subsequently milling the thin foil with a 5 kV current at 68 pA. The electron transparency was monitored by an Everhart-Thornley SE detector and using a 5 kV electron beam. After achieving the electron transparency, the thin foil was rapidly polished using a low energy 5 kV current at 10 pA to reduce the

Table 1. Chemical composition of magnetite.

N	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	MnO	CoO	NiO	Total
1	0.04	0.10	69.49	30.58	0.57	0.16	0.03	100.96
2	0.04	0.05	69.92	30.71	0.60	0.16	0.04	101.53
3	0.03	0.11	69.88	30.74	0.57	0.17	0.04	101.53
4	0.05	0.14	69.93	30.81	0.58	0.16	0.03	101.71
5	0.04	0.14	69.77	30.71	0.60	0.15	0.02	101.44
6	0.04	0.10	69.66	30.63	0.59	0.17	0.03	101.22
7	0.04	0.14	69.51	30.59	0.60	0.14	0.04	101.08
8	0.04	0.12	69.39	30.50	0.58	0.17	0.06	100.88
9	0.04	0.12	69.53	30.62	0.56	0.17	0.02	101.06
10	0.04	0.12	69.60	30.61	0.59	0.17	0.03	101.15
11	0.04	0.15	69.29	30.49	0.58	0.16	0.05	100.76
13	0.04	0.16	69.17	30.47	0.57	0.16	0.03	100.61
14	0.04	0.13	69.20	30.44	0.59	0.16	0.03	100.59
15	0.04	0.13	69.44	30.60	0.56	0.17	0.02	100.95
20	0.04	0.16	69.43	30.56	0.58	0.17	0.04	100.98
22	0.03	0.07	69.62	30.61	0.58	0.17	0.02	101.11
23	0.04	0.13	69.61	30.61	0.59	0.16	0.05	101.18
24	0.04	0.12	69.50	30.57	0.59	0.17	0.03	101.02
26	0.03	0.03	69.35	30.54	0.54	0.17	0.01	100.66
28	0.04	0.09	69.54	30.56	0.61	0.16	0.02	101.02
Atoms per formula unit								

N	Al	Cr	Fe3+	Fe2+	Mn	Co	Ni
1	0.00	0.00	2.00	0.98	0.02	0.00	0.00
2	0.00	0.00	2.00	0.97	0.02	0.00	0.00
3	0.00	0.00	2.00	0.98	0.02	0.01	0.00
4	0.00	0.00	1.99	0.98	0.02	0.00	0.00
5	0.00	0.00	1.99	0.98	0.02	0.00	0.00
6	0.00	0.00	1.99	0.97	0.02	0.01	0.00
7	0.00	0.00	1.99	0.98	0.02	0.00	0.00
8	0.00	0.00	1.99	0.97	0.02	0.01	0.00
9	0.00	0.00	1.99	0.98	0.02	0.01	0.00
10	0.00	0.00	1.99	0.97	0.02	0.01	0.00
11	0.00	0.00	1.99	0.97	0.02	0.01	0.00
13	0.00	0.00	1.99	0.98	0.02	0.01	0.00
14	0.00	0.00	1.99	0.97	0.02	0.00	0.00
15	0.00	0.00	1.99	0.98	0.02	0.01	0.00
20	0.00	0.00	1.99	0.98	0.02	0.01	0.00
22	0.00	0.00	2.00	0.98	0.02	0.01	0.00
23	0.00	0.00	1.99	0.97	0.02	0.00	0.00
24	0.00	0.00	1.99	0.98	0.02	0.01	0.00
26	0.00	0.00	2.00	0.98	0.02	0.01	0.00
28	0.00	0.00	2.00	0.97	0.02	0.00	0.00

SiO_2 is always below 0.5wt. %

TiO_2, V_2O_3, MgO and ZnO are below detection limit.

amorphization until a final thin foil thickness of ~90 nm was attained. Subsequently, the thin foil was undercut with a 30 kV at 2.5 nA current, lifted out, and transferred from the sample to a TEM grid using an OmniProbe nano-manipulator with a tungsten tip. To weld the thin foil to the tungsten tip and the TEM grid, an ion-beam assisted Pt deposition was performed.

A FEI Titan G2 transmission electron microscope (TEM) equipped with Field Emission gun XFEG was used to analyze the thin-foil at the Centro de Instrumentación Científica of the University of Granada, Spain. The FEI Titan G2 microscope is equipped with 4 energy dispersive analyses of X-rays (EDX) detectors (FEI microanalysis Super X) and a high-angle annular dark-field detector

(HAADF). This FEI Titan G2 microscope also includes a spherical aberration corrector for the objective lens. Selected mineral areas of interest sampled within the thin-foil were imaged by the FEI Titan G2 microscope using a combination of high-angle annular dark-field (HAADF) to obtain Z high contrast images, and High-Resolution Transmission Electron (HRTEM) images to characterize the texture of the grains and to properly define the ordering of the mineral aggregates. All these images were treated using the Digital Micrograph® software in its Version 1.71.38 while maps were processed with the VELOX® software package. The FEI Titan G2 was running at 300 kV working conditions while HRTEM images were acquired using Gatan CCD Camera. Elemental maps images were also processed using the VELOX® software.

3. Results

Two iron-rich oxide and two silicate glass spherules were recovered from two chromitites bodies hosted in the upper mantle section the Golyamo Kamenyane and Yakovitsa ultramafic massifs, in southern Bulgaria (Figure 1). These rocks belong to the Rhodopean Ophiolite Association (Kolcheva *et al.*, 2000), which correspond to a lithospheric section formed a mid-oceanic ridge that evolved to an island arc/back-arc setting in a supra-subduction zone (Colás *et al.*, 2013).

The largest iron-rich oxide spherule (~75-175 μm) was found in the Yakovitsa chromitite (Figure 2a-2l). It consists of an interlocking polygonal structure made up of micro-crystallites of magnetite with junctions, which are filled by a finely-grained symplectite of magnetite and amporphous Si glass
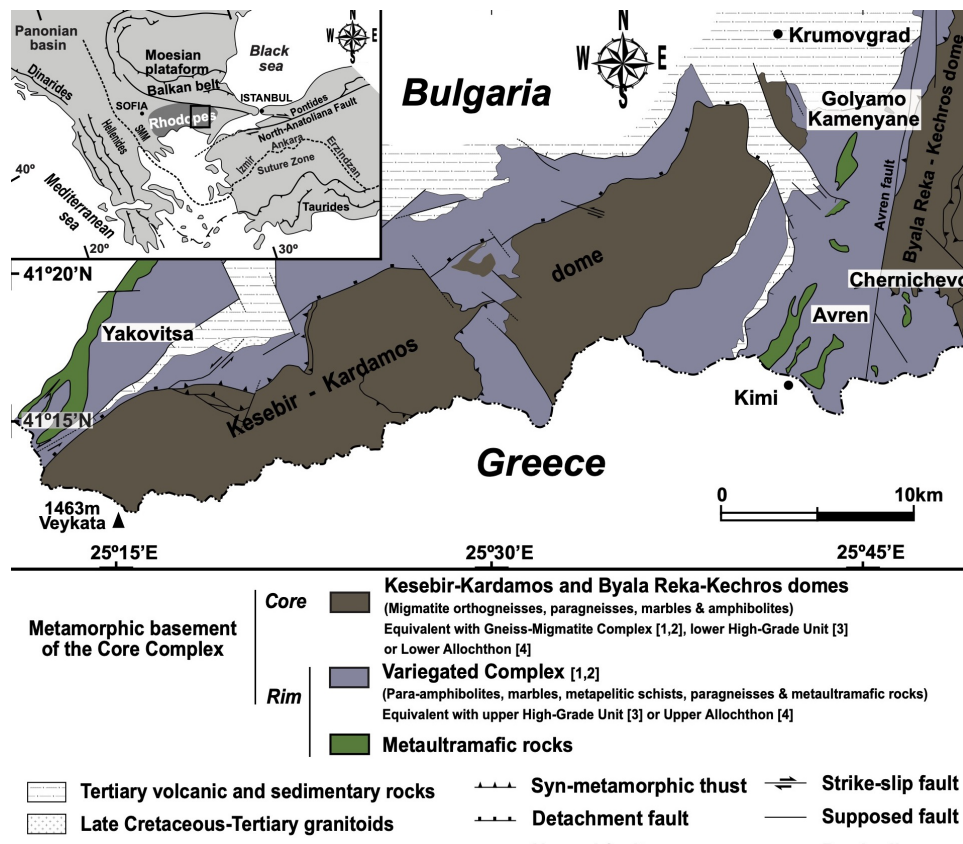

Figure 1 Simplified geological map of the Eastern Rhodope (adapted from Bonev, 2006) showing the localization of the ultramafic massifs hosting the chromitite bodies investigated in this work. Equivalence keys: 1 (Kozhoukharov *et al.*, 1988), 2 (Haydoutov *et al.*, 2001), 3 (Bonev, 2006), and 4 (Janák *et al.*, 2011). Legends are in all cases inset in the figures.

with trace amounts of P (Figure 2a-2l). Single-spot analyses obtained by EMPA show relatively homogenous composition of magnetite across the whole sphere with up to 93.47 wt.% FeOt, minor Mn (0.54-0.61 wt%), CoO (0.14-0.17 wt%), Cr_2O_3 (0.03-0.16 wt%), Al_2O_3 (0.03–0.05 wt%), NiO (0.01-0.06 wt%), SiO_2 (<0.5 wt%), and no TiO_2, MgO or CaO (Table 1). The smaller iron-rich oxide spherule identified in Golyamo Kamenyane (Figures 3a-3c) consists of dendritic magnetite (Fe_2O_3) microcrystals within a wüstite (FeO) groundmass as determined by micro-RAMAN and FESEM-

EDX analysis collected from the spherule surface (Figures 3d-3f). The discrete crystals of magnetite are small (<5 μm) faceted-equant grains with cubic arrangement perpendicular to (111) crystal faces (Figure 3b), whereas rosaries of sub-micrometric spherules of magnetite occur widespread in the wüstite groundmass (Figure 3c).

The glassy spherules are both colorless with a smooth surface (Figures 4a and 4b) relatively homogenous in composition dominated by SiO_2 (~41 wt.%), CaO (31-34 wt-%) and Al_2O_3 (14-15 wt%), and lesser amounts of FeOt (~7 wt.%), MgO
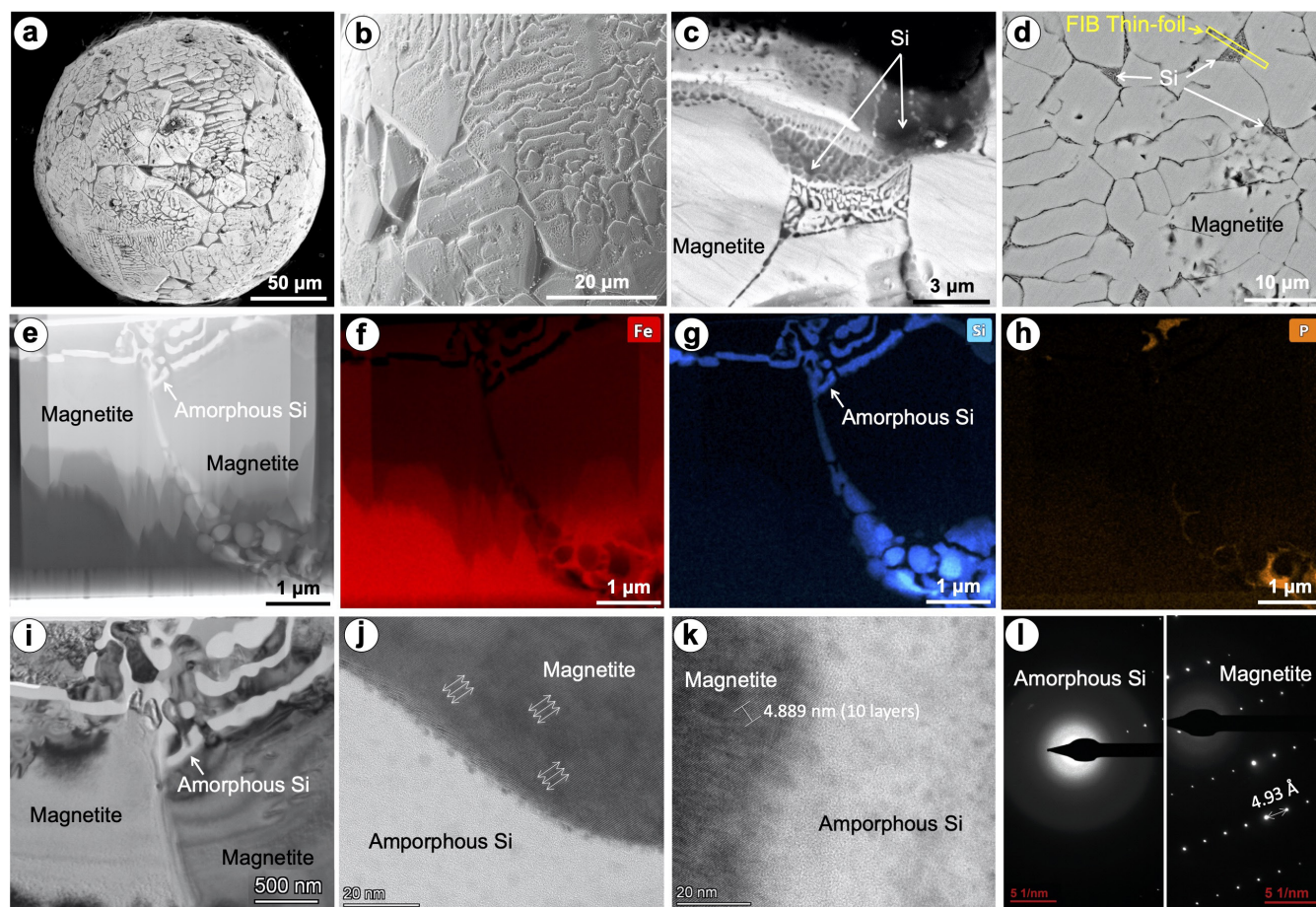
Figure 2 Microphotographs of the iron spherule recovered from the Yakovitsa chromitite. (a-c) and (d) are images of the microtexture of the spherule collected by FE-SEM previously and after polishing, respectively. (e-h) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and corresponding TEM-EDS elemental map of the FIB thin foil (see location in (d)). (i-k) High-resolution (HR)-TEM and high-magnification HRTEM images of the anatomy of the contact between magnetite microplates and symplectite amorphous silica. (l) Selected area electron diffraction (SAED) image showing the amorphous nature of the silica sympletitice and crystallinity of magnetite.

RESULTS

(2-4 wt.%) as well as Ti and K < 1.5 wt.% (see EDX inset in Figure 4). These two spherules were partly smashed during the mounting process, reveling internal continuity of the vitreous structure with the typical conchoidal fractures of glassy materials (Figures 4c and 4d). The spherule recovered from the Golyamo Kamenyane chromitite displays shrinkage features such as bubble-like vesicles now filled with a suite of secondary minerals including magnetite, quartz, rutile or mixtures of them (Figure 4b). Under high magnification magnetite exhibit rounded to octahedral-habit, whereas quartz is prismatic and rutile is needle-like to acicular crystals grown perpendicular to the surface of the vesicle.
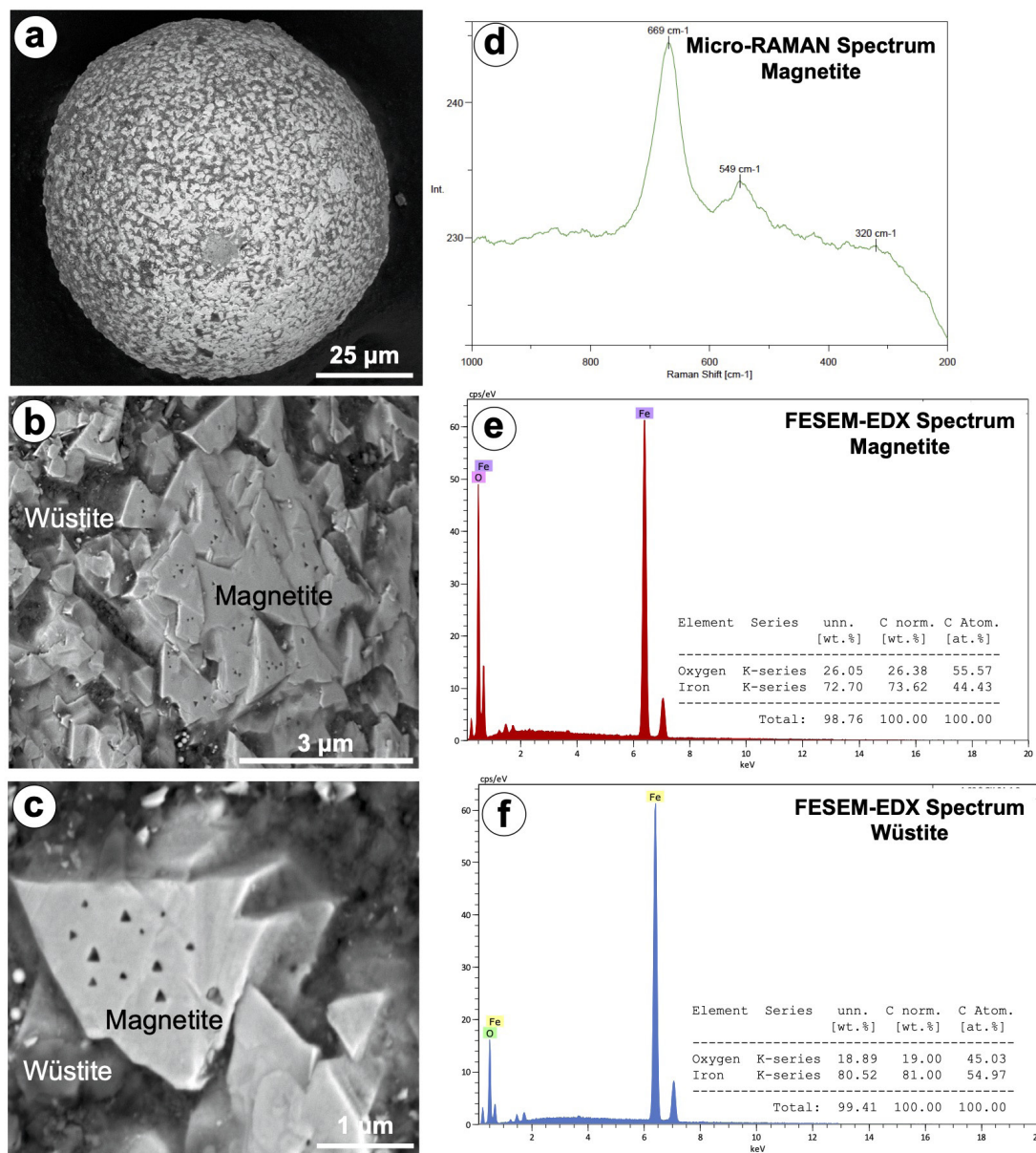

Figure 3 Microphotographs of the iron spherule recovered from the Golyamo Kamenyane chromitite. (a-b) Secondary electron (SE) FE-SEM images of the unpolished spherule. (d-f) Representative spectrums of magnetite and wüstite collected micro-RAMAN and FESEM.

4. Discussion and concluding remarks

4.1. IDENTIFYING SPHERULES IN MANTLE-DERIVED ROCKS

As noted above, metallic-silicate-oxide spherules found in natural rocks may have both natural and anthropogenetic origins. Some textural (magnetite, rutile and quartz filling voids in the glassy spherule) and chemical features (very low Mn in the iron-rich spherule) of the spherules from the Bulgarian chromitites clearly rules out contamination by man-made spherules (Sulovsky, 2002; Zhang *et al.*, 2014; Shetye *et al.*, 2019) during mineral separation processes.

Spherules having structures and textures similar to ours - dendrite magnetite with interstitial silicate glass or wüstite groundmass and silicate glass only; Figures 2-4 - have not been reported yet from ophiolitic mantle-derived rocks. Most spherules documented in peridotites and associated chromitites from ophiolites (i.e., Tibet, Ray-Iz and Oman) consist of Ni-free native iron (α-Fe) with cortex of dendritic wüstite, both having very small quantities (<<1 wt.%) of Mn, Ti and Si (Bai *et al.*, 2004; Robinson *et al.*, 2004; Xu *et al.*, 2015; Griffin *et al.*, 2016). Some spherules documented from Tibetan chromitites exhibit an additional thin layer of hematite separating the iron core and
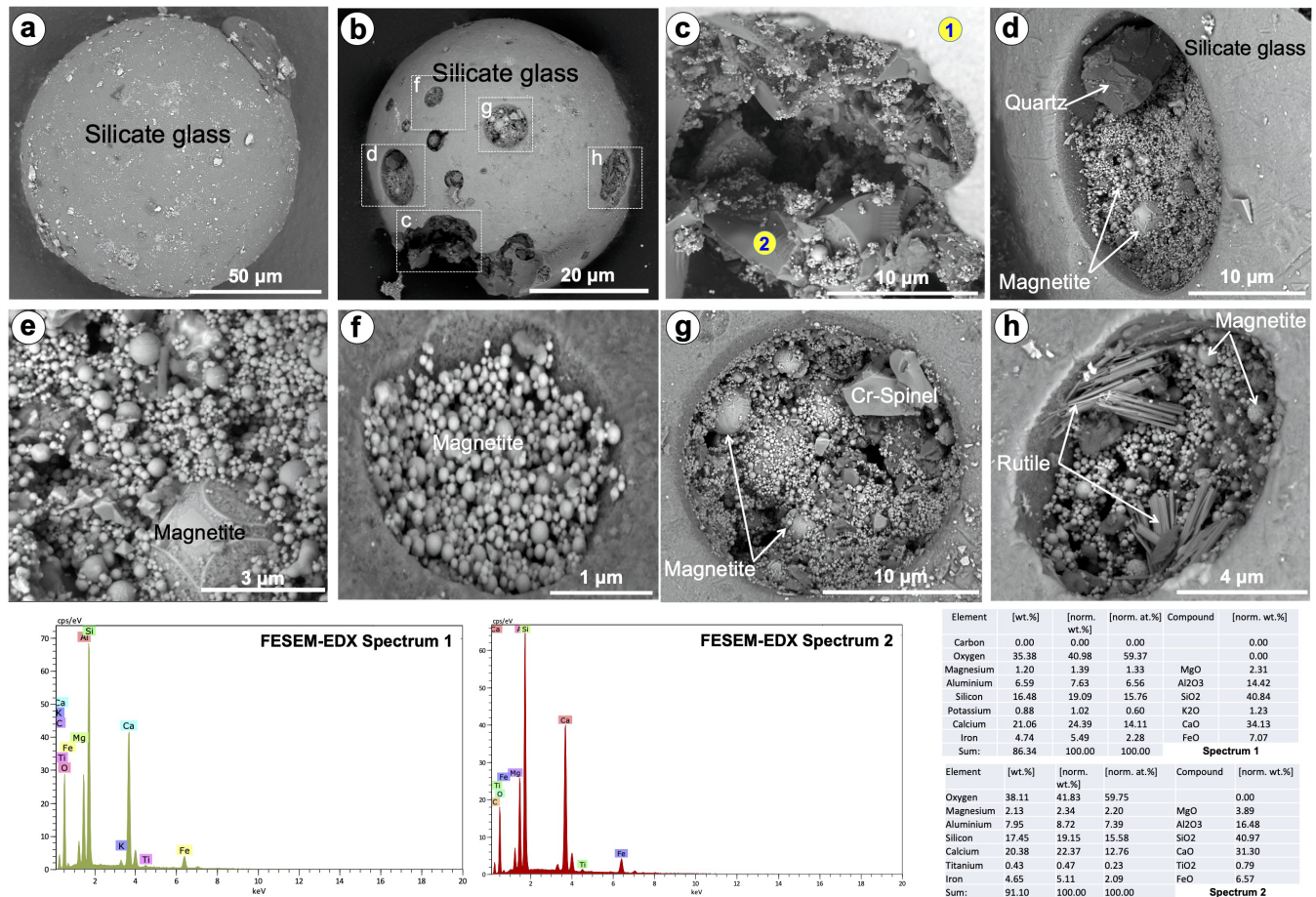
Figure 4 Microphotographs collected by FESEM in SE mode of the glassy spherules recovered from the Yakovitsa (a) and Golyamo Kamenenyane (b-h) chromitites. Representative FESEM-EDX spectrum of the glass are inset in the figure.

the wüstite rim (Xu *et al.*, 2015), whereas some others from Ray-Iz have iron core with drop-like inclusions wüstite, Fe–Ti alloys and/or silicate glass with up to 39 wt.% TiO_2, 19 wt.% SiO_2, 4 wt.% Al_2O_3, 22 wt.% FeO, 8 wt.% MnO, 6 wt.% Ca and 1 wt.% K_2O (Yang *et al.*, 2015). A subset of the spherules identified *in-situ* in chromites from Tibet consist of Ni-Fe (formula $Ni_{7.4} Fe_{2.6}$; Xu *et al.*, 2009) and host inclusions of pentlandite, periclase and magnesium silicates.

These spherules documented in mantle-derived ophiolitic rocks were related to fluids/melts of very high temperature (>1400-1500 ºC) and low fO_2 (well below IW buffer) operating in the lower mantle or the Mantle Transition Zone (i.e., MTZ > 610 km; Xu *et al.*, 2015; Griffin *et al.*, 2016). This interpretation was based on two assumptions: (1) the assemblage iron + wüstite was also found in diamonds of deep-seated peridotites and kimberlites (e.g., Xu *et al.*, 2015), and (2) metallic-silicate-oxide spherules belong to the Super-reducing (SuR) mineral assemblage (e.g., moissanite, carbides, nitrides and silicides) that is usually found together with minerals that typically form at UHP (e.g., diamond and coesite) in these mantle rocks. Pioneering works suggested a common origin of the SuR and UHP during chromitite crystallization from high-Cr melts within the lower part of the upper mantle or MTZ (Yang *et al.*, 2007; Zhou *et al.*, 2014; Zhang *et al.*, 2016) or metamorphism of recycled chromitites at these high depths (McGowan *et al.*, 2015; Griffin *et al.*, 2016). However, subsequent works (e.g., Xiong *et al.*, 2017) suggested that SuR minerals could be incorporated into exhuming peridotites (and associated chromitites) that already had UHP by metasomatic slab-derived $CH_4 \pm H_2$ fluids, or mantle melts that were supplied with such component. Moreover, all spherules identified in these mantle-derived rocks, except the Ni-Fe bearing isolated inclusions in chromite from Tibetan chromitites, were found in mineral separates, therefore do not provide the necessary direct connection between the spherules and the other minerals of the SuR-UHP to confirm their true mantle origin.

In addition, subsequent works showed that SuR-UHP minerals might also form during low-pressure partial hydration of oceanic lithosphere (Farré-de-Pablo *et al.*, 2019; Pujol-Solà *et al.*, 2018). Thus, a need for the inquiry on the generalized deep mantle-related origin of for the alleged SuR-UHP assemblage has arisen.

The spherical morphologies along with the droplet-like shape of wüstite and/or silicate glass within iron cores reported in spherules from Ray-Iz are consistent with surface tension of unmixing metallic, oxide and silicate melts at high-temperature. However, such mechanism itself cannot satisfactorily explain the presence of silicate glass found as both inclusions within native iron and interstitial to dendritic magnetite and/or wüstite. Rather, silicate glass suggests melts quickly frozen (quenched) as these are non-equilibrium materials that form due to fast kinetics preventing complete crystallization after melting with extremely high cooling rates (i.e., in the order of 10^7 ºC/min for hyper-quenched glasses; McCloy, 2019). Therefore, it is unlikely that those spherules containing glasses were originated *in-situ* within the Earth's mantle. In fact, silicate glasses in mantle rocks can only be attributed to trapped interstitial melts that have quenched during fast volcanic eruptions (O'Reilly and Griffin, 2012). Interestingly, the glass in these spherules from Ray-Iz has higher Ti than glasses in analogous volcanic and cosmic spherules. Its chemistry is, however, similar to that of silicate-titanium-iron spherules reported from the Colônia impact crater in Brazil (Veláquez *et al.*, 2021). However, these spherules lack of sculpturing or impact marks (microcraters, pits with radial cracks and star-shaped pit) as those of impact-related origin.

The patterns of iron nuclei and oxide cortex or dendritic magnetite in wüstite groundmass documented in the spherules from Tibet and Ray-Iz and Golyamo Kamenyane ophiolites are very similar to those reported in I-type cosmic spherules (Genge *et al.*, 2017). In contrast, the microtexture of dendritic magnetite within Si-bearing glass of the Yakovitsa spherule has been identified in volcanic

DISCUSSION AND CONCLUDING REMARKS

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(e.g., Ignimbrites of Southern Primorye in Rusia; Grebennikov, 2011) and G-type cosmic spherules (Folco and Cordier, 2015). A common feature of all spherules found in ophiolitic mantle rock is that both magnetite and wüstite have Ni contents below 1.0 wt.%. Low Ni in oxides is a common feature of cosmic spherules where Ni was separated from the silicate-oxide melts towards metallic beads due to siderophile attraction display (Genge *et al.*, 2017). In fact, a population of spherules reported from Tibetan chromitites still contain Ni-Fe beads or are solely Ni-Fe spherules, similarly to the vast majority of I-type cosmic spherules reported in the geological record (Folco and Cordier, 2015; Genge *et al.*, 2017). Nevertheless, cosmogenic nuclide and noble gas analyses are not available for spherules associated with mantle peridotite and chromitites to confirm their extraterrestrial or terrestrial origin. This is clearly a green field for future research.

Silicate glass spherules from our chromitites exhibit some common features with silicate-dominant volcanic and V-type cosmic spherules, including: (1) spherical morphology, with smooth external surface and internal conchoidal fractures as is typical for quenched silicate-droplet glass, (2) empty vesicles (now filled with secondary minerals) that may have been produced by degasification or dissolution of pre-existing metal beads. However, their markedly higher Al and Ca but lower Mg distinguish them from cosmic ones. Overall, the concentration of all the analyzed elements overlaps that of terrestrial basic basaltic glasses (McCloy, 2019; Cicconi and Neuville, 2019), suggesting their possible volcanic-related origin.

4.2. RECYCLING SPHERULES IN THE UPPER MANTLE?

Shi *et al.* (2011) suggested an extraterrestrial origin for a suite of iron spherules they recognized in jadeitites from the Myanmar ophiolite. In these spherules with Fe isotopic composition overlapping I-type cosmic spherules, core of native iron is also overgrown by a rim made up of dendritic crystal of wüstite. This discovery shows

that cosmic spherules could remain stable under low-temperature and high-pressure conditions prevailing upon subduction, and therefore might be found in rocks related to slab-derive sediments in subduction zones. Interestingly, some spherules from Ray-Iz exhibit an identical pattern, raising the possibility that cosmic spherules (and by extension volcanic ones) now found in peridotites and chromitites from ophiolites could represent part of sediments that were incorporated into the upper mantle via subduction. The recycling of crustal material in the mantle and return pathways to the Earth's surface has been already tracked by xenocrystal zircons inherited from continental sources in supra-subduction zone ophiolitic and juvenile intra-oceanic volcanic arc rocks (Proenza *et al.*, 2018). In this scenario, it is expected that the spherules had experienced a series of events since their deposition in the deep sea including: modification during fly, alteration during diagenesis and transport with the oceanic slab into the subduction zone, high P/T metasomatism/metamorphism, heating by carrying fluids and melts involved in mantle metasomatism and chromitite formation, and final exhumation. However, all the spherules identified in ophiolitic mantle rocks are well-preserved as their shapes and chemical composition were not obviously altered. Then, how can these spherules could be transported and recycled into the shallow oceanic mantle without affection?

Subducted slabs can transport significant volumes of sediments to depths greater than 50 km (Scholl and von Huene, 2009) and these, in turn, may be transferred to the mantle wedge by (1) fluids/melts channelized in melt conduits or fractures (González-Jiménez *et al.*, 2017), and/or (2) detachment and buoyancy-driven diapiric up flow of plumes of slab-derived sediments (Gerya and Yuen, 2003). The first mechanism links the transfer of slab-derived spherules to the introduction of silica- and alkali-rich fluids/melts due to the dehydration/ anatexis of subducted sediments through fractures in mantle peridotites; it could be linked to mechanism similar to those transferring spherules to jadeitites as observed in the Myanmar ophiolite.

The second mechanism could be related with the cold plumes –partly molten crustal (including sediments, continental crust and basalts) and mantle rocks mixed on length scales from a few tens of meters to hundreds of kilometers – contributing to mantle metasomatism and chromitite formation (González-Jiménez *et al.*, 2017; Proenza *et al.*, 2018). In these two scenarios, the equilibration of spherules with surrounding rocks and melts might be inhibited by their rapid transfer through fractures or by porous flow in small melt pockets from the melting source to a new site in, or their inclusion in shielding minerals like pyroxene, olivine or during melt transport. The incorporation of such type of inherited xenocrystic pyroxenes and olivine have been largely reported in chromitites and melt pockets of peridotites from ophiolites (e.g., Borisova *et al.*, 2012; Griffin *et al.*, 2016).

Contributions of authors

JMGJ and IS designed the experiment and carried out the analytical work. JMGJ wrote the manuscript which was revised and intellectually improved by the input of TNK and FG.

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Conflicts of interest

The authors declare no conflict of interest.

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