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Cosmic spherules from the Ordovician of Argentina

G. G. VOLDMAN[1]*, M. J. GENGE[2], G. L. ALBANESI[1], C.R. BARNES[3] and G. ORTEGA[1]
[1] *CONICET—Museo de Paleontología, Universidad Nacional de Córdoba, Córdoba, Argentina*
[2] *Department of Earth Science and Engineering, Imperial College London, London, UK*
[3] *School of Earth and Ocean Sciences, University of Victoria, Victoria, BC, Canada*

The discovery of magnetic spherules in acid-insoluble residues from conodont samples encouraged a systematic search for Ordovician micrometeorites from northwestern Argentina. Some 220 melted micrometeorites were recovered from the magnetic fraction of six samples (total rock weight: 23 kg) from the Cordillera Oriental (Santa Rosita Formation) and 17 from five samples (total rock weight: 8.9 kg) from the Argentine Precordillera (Las Aguaditas, Gualcamayo and Las Vacas formations). The specimens resemble I-type cosmic spherules, in their chemistry and distinct dendritic and polygonal crystalline structures. They represent a flux of micrometeorites several orders of magnitude greater than present. The wide differences in spherule abundance between the Precordillera and the Cordillera Oriental samples could reflect uncertainties in the sedimentary rates or temporal variations in the flux of extraterrestrial matter to Earth. The micrometeorite-bearing formations span the late Tremadocian to the late Darriliwian (~480–460 Ma), which is consistent with a period of elevated flux of extraterrestrial material, as recorded several thousand kilometres away from coeval horizons in Scotland, Sweden and central China. Copyright © 2012 John Wiley & Sons, Ltd.

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1. INTRODUCTION

Fluctuations in the influx of extraterrestrial materials to Earth play an important role in the weak equilibrium between the oceans, atmosphere, climate, and life (e.g. Álvarez *et al*., 1980). The extraterrestrial flux is assumed to have been more or less constant except for a few peaks in the accretion rates, such as at the K/T boundary. Currently, the principal component of extraterrestrial matter accreted by the Earth is cosmic dust in the size range of micrometeorites, nearly 1000 times more by mass than meteorites (e.g. Love and Brownlee, 1993; Taylor *et al*., 1998). The flux peaks are intimately related to gravity perturbations of the orbits of the comets and catastrophic disruptions in the asteroid belt (e.g. Matese *et al*., 1995; Nesvorný *et al*., 2009).

The discovery of numerous fossil meteorites in Middle Ordovician marine limestones from southern Sweden indicates an increase in the flux of meteorites up to two orders of magnitude greater than today for that period (Schmitz *et al*., 2001). A Middle Ordovician increase in the meteorite flux is further supported by an iridium anomaly, osmium isotope data and by the distribution of sediment-dispersed extraterrestrial (ordinary chondritic) chromite grains from Sweden and central China (Schmitz *et al*., 1997; Cronholm and Schmitz, 2010). Accordingly, Dredge *et al*. (2010) determined a flux of micrometeorites one to two orders of magnitude greater than present in Dapingian (~472–468 Ma) limestone samples from the Durness Group in Scotland.

The extraordinary Middle Ordovician increase in the flux of extraterrestrial matter to Earth is thought to result from the catastrophic disruption of the L-chondrite parent body in the asteroid belt at 470 ± 6 Ma (Greenwood *et al*., 2007; Korochantseva *et al*., 2007). Up to 25% of all meteorites that reach Earth even today show gas retention ages referable to this breakup event, probably one of the most important in the late history of the solar system (Schmitz *et al*., 2001). Nesvorný *et al*. (2009) estimated that approximately five large terrestrial impacts are likely to have occurred within ≈2 million years after the family-forming meteorite breakup. The high meteorite influx probably produced mass wasting at continental margins on a global scale (Parnell, 2009; Alwmark *et al*., 2010). Additionally, it could have tremendous implications for the Earth's biosphere; for instance,

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*Correspondence to: G. G. Voldman, Museo de Paleontología, Universidad Nacional de Córdoba, Av. Velez Sarsfield 249, Córdoba X5000FCO, Argentina. E-mail: gvoldman@efn.uncor.edu

Schmitz *et al*. (2008) speculated that the large quantities of cosmic material accreted by the Earth at ~470 Ma may have perturbed the climatic/biologic conditions on the Earth, leading to the Great Ordovician Biodiversification Event (GOBE). Furthermore, the Ordovician was also a period of widespread magmatism, terrane accretion and continental or back-arc rifting (Finney and Berry, 2010 and references therein), affecting the biosphere as well.

The discovery of magnetic spherules in acid-insoluble residues from conodont samples by the present authors encouraged a systematic search for Ordovician micrometeorites. This study analyses the occurrence of cosmic spherules from Precordillera and Cordillera Oriental of northwestern Argentina (Figure 1), in an attempt to understand the effects of the Ordovician cosmic events in the southwestern Gondwanan continental margin.

2. PREVIOUS STUDIES OF MICROMETEORITES

Micrometeorites are extraterrestrial dust particles between 10 μm and 1 mm in size recovered from the Earth's surface (Rubin and Grossman, 2010). Extraterrestrial dust is subject to a range of heating during atmospheric entry depending on entry velocity and entry angle allowing a proportion of particles to survive to be recovered from the Earth's surface (e.g. Love and Brownlee, 1991). Melted micrometeorites formed as largely molten droplets during atmospheric entry are known as cosmic spherules and comprise 50%–75% of micrometeorites 50–100 μm in size (Genge *et al*., 2008). The majority of cosmic spherules are olivine- and glass-dominated spheres (S-types). However, spheres dominated by the iron oxides magnetite and wüstite (I-types) comprise 1%–5% of recent spherules.

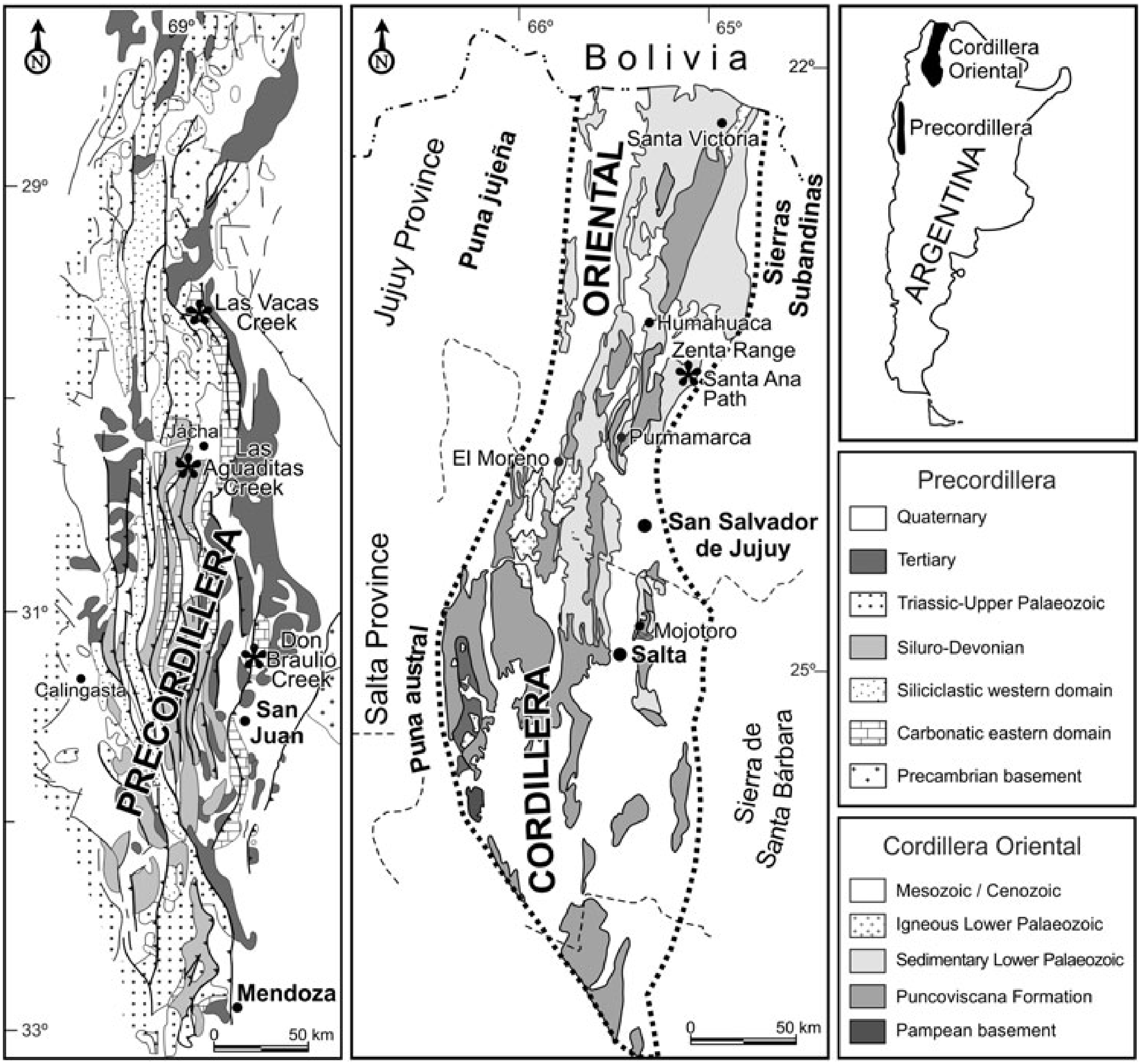

Figure 1. Location maps of the study areas. The asterisks indicate the spherules localities.

Measurements of the present-day flux of extraterrestrial dust from microcraters on satellites (Love and Brownlee, 1993), and from collections of micrometeorites (Taylor *et al*., 2000), suggests an accretion rate of ~10 000 t a^{-1}, significantly larger than the annual influx of meteorites (2.9–7.3 t a^{-1} according to Bland *et al*., 1996). The majority of present-day micrometeorites are thought to have been extraterrestrial dust particles prior to atmospheric entry, rather than debris separated from larger meteoroids during their passage through the atmosphere.

Recent micrometeorites (<2 Ma) have been collected in large numbers from Antarctic ice (Maurette *et al*., 1991) and traps (Rochette *et al*., 2008), and from deep-sea sediments (Brownlee *et al*., 1984). Antarctic collections contain abundant pristine unmelted and partially melted micrometeorites, whilst deep-sea collections are dominated by spherules and rare partially melted particles. Micrometeorites have also been recovered from a range of sediments in the geological column including: Jurassic hardgrounds (Taylor and Brownlee, 1991), Triassic pelagic sediments and evaporites (Davidson *et al*., 2007; Onoue *et al*., 2011), and Ordovician carbonates (Schmitz *et al*., 1997; Cronholm and Schmitz, 2010; Dredge *et al*., 2010).

3. GEOLOGICAL SETTING

Two important depocentres containing Ordovician fossiliferous rocks from the Andes of Argentina are presently analysed: the Central Andean Basin, situated in northwest Argentina and extending into Chile, Bolivia and Perú, and the Precordillera Basin (as part of the Cuyania composite terrane), located along the eastern foothills of the southern Central Andes and limited to the south by the northern extension of Patagonia (Ramos, 2009) (Figure 1).

Outcrops of the Central Andean Basin are superbly exposed in the Cordillera Oriental, a thick-skinned mostly east-vergent thrust system limited to the west by the Puna plateau and to the east by the Sierras Subandinas. The stratigraphy of the Cordillera Oriental reflects relatively shallow-marine environments ranging from outer shelf to shoreface, rarely dominated by tidal complexes, in contrast to the deep-water setting of the Puna (Astini, 2003). In particular, in the Zenta Range, the Lower Ordovician strata are over 3000 m in thickness (Santa Victoria Group), yet the sedimentary and palaeontological aspects of this succession are scarcely known, lacking clear stratigraphic subdivisions. In this area, the sedimentary succession exhibits rhythmic monotonous series of shaly intervals punctuated by clastic wedges, which correspond to prograding coastal systems dominated by wave activity and storms towards the top (Astini, 2008).

The Precordillera of NW Argentina comprises a high-level fold-and-thrust belt, mostly composed of Cambrian to Carboniferous strata, triggered by flat-slab subduction of the Nazca Plate in Neogene times (Ramos *et al*., 2002). The Eastern and Central domains of the Precordillera involve an important passive margin carbonate platform, Cambro-Ordovician in age, which is covered by siliciclastic foreland deposits (Astini, 2003). The Western Precordillera exhibits deeper water environments, with slope to ocean floor deposits, which include pillow lavas and mafic-ultramafic bodies in the westernmost sections. It is affected by a very low-grade metamorphism that locally reaches greenschist facies and shows evidence of a complex deformation and metamorphism during the Ordovician and Silurian to Devonian times (Buggisch *et al*., 1994; Robinson *et al*., 2005; Voldman *et al*., 2010)

3.1. Palaeogeography

The regional tectonic evolution of the western margin of Gondwana (Figure 2) reveals a long history of plate convergence since the Neoproterozoic rifting of Rodinia until the late Palaeozoic termination of the Terra Australis Orogen, which led to the final assembly of Pangaea. The Pacific margin of South America is mostly characterized by a siliciclastic platform, with rift-drift transitions gradually

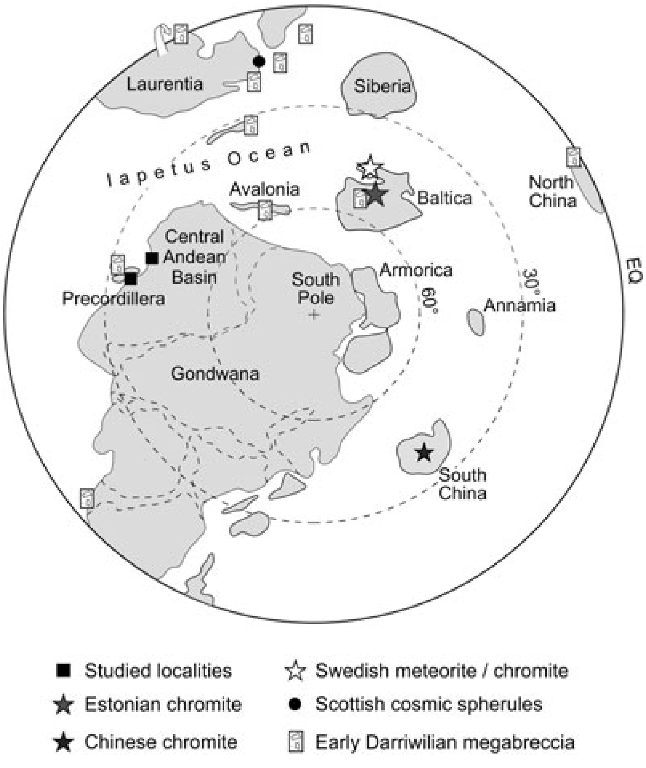

Figure 2. Palaeogeographic reconstruction of the Southern Hemisphere at ~470 Ma including the study sites [modified from Cocks and Torsvik (2002) and Parnell (2009)]. Chromite data from Alwmark *et al*. (2010) and Cronholm and Schmitz (2010), Scottish cosmic spherules from Dredge *et al*. (2010).

younging to the north and deposited over an autochthonous basement from Venezuela to northwestern Argentina (Cawood, 2005). However, the sedimentary sequences are largely obliterated by later tectonic events related to the building of the present Andean margin. The general asymmetric configuration and the stratigraphy of the neighbouring regions across the Central Andean Basin suggest an evolution compatible with a broad Ordovician foreland basin (Astini, 2003).

Further south, the early Palaeozoic history of the southern Central Andes is different, despite the striking synchronicity of the magmatic and tectonic processes that encompassed the whole proto-Andean margin of Gondwana (e.g. Ramos, 2008). Major changes in its basin configuration and palaeobiogeographic affinities were classically related to stages of rifting, drifting and collision of the Precordillera with the South American margin (Figure 2). The drowning of the Precordillera carbonate platform in the Middle Ordovician was associated with an important palaeogeographical rearrangement of depocentres and source areas. A large influx of fine-grained clastics filled rapidly subsiding marine basins, punctuated by local deposition of olistostromes, debris flows, conglomerates, and turbidites (e.g. Astini *et al*., 1995; Keller, 1999). In the western slope facies of the Precordillera, local infill of Cambrian-Ordovician olistoliths record gravitational collapse of the passive continental margin. This mass wasting could be either related to earthquake and tsunami-driven slope failure caused by bombardment of the Earth's surface with large meteorites over a period of almost 10 Ma (Parnell, 2009) or more probably, to instability of slopes related to plate-tectonic processes (Alonso *et al*., 2008; Meinhold *et al*., 2011). According to the most supported hypothesis, the Precordillera drifted from a low-latitude position in the Cambrian to collide against the proto-Andean margin of Gondwana by the Early-Middle Ordovician (Thomas and Astini, 2003; Voldman *et al*., 2009). The time of the collision is supported by the particular geographic distribution of endemic faunas and the widespread distribution of Hirnantian glacial deposits in Gondwana, which overlaps the Precordillera and the Central Andean Basin (Figure 3) (Benedetto *et al*., 2009; Albanesi and Bergström, 2010).

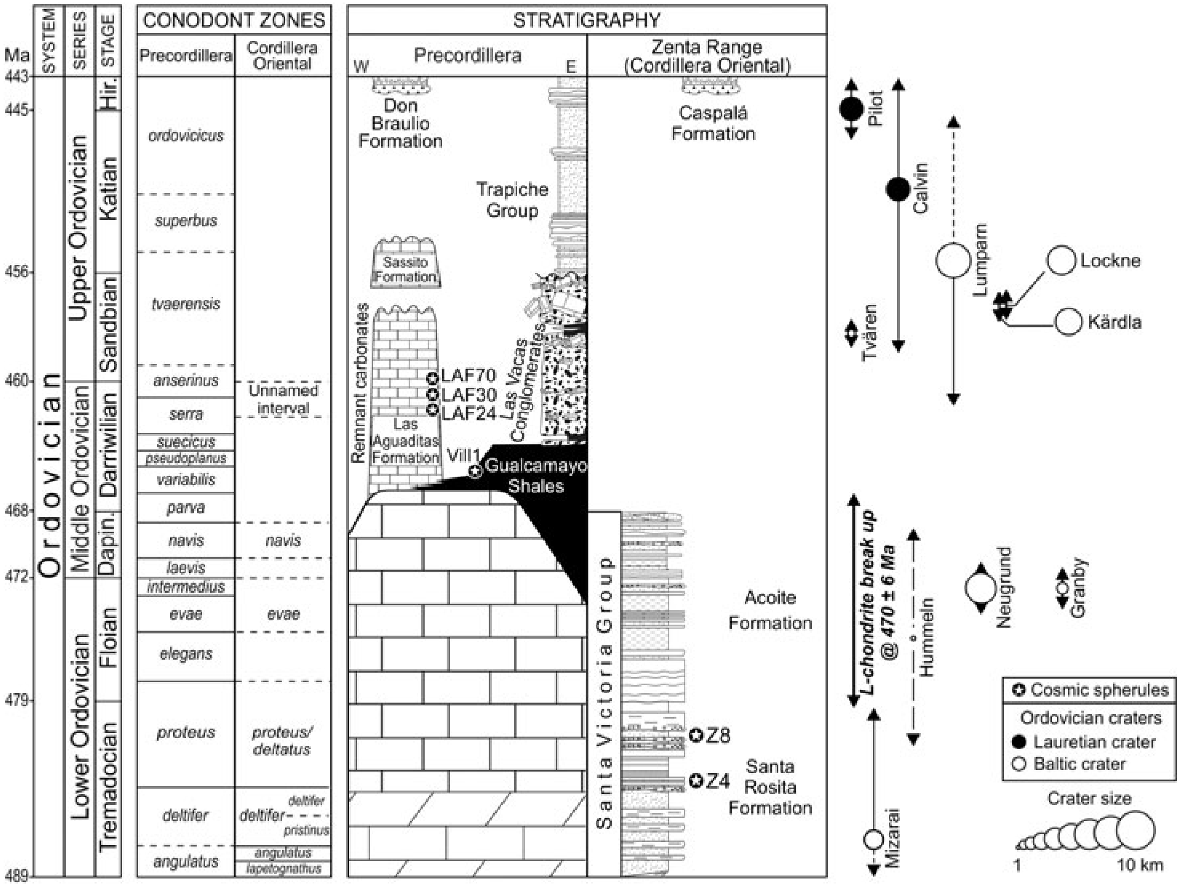

Figure 3. General stratigraphy of the Ordovician system from the Argentine Precordillera and the Zenta Range (Cordillera Oriental). Position of the cosmic spherules and world impact craters from Alwmark *et al*. (2010) and Earth Impact Database (2011). IUGS time scale (Ogg *et al*., 2008). Dapin., Dapingian; Hir., Hirnantian.

4. ANALYTICAL METHODS

All of the rock samples were collected as whole specimens to minimize possible contamination, employing an Estwing pick. The rock samples were processed in the Laboratory of Micropaleontology of the Universidad Nacional de Córdoba, following the standard techniques employed to remove the carbonate content and recover conodonts (Stone, 1987). This way, the rock samples were fragmented in a metallic press to 5–10 cm pieces, in order not to modify the original taphonomic information, then washed with tap water to remove loose particles, weighed, and digested in 10% acetic acid under a fume cupboard. All containers were kept covered in an effort to eliminate dust contamination and retain toxic gases. The insoluble residue was then separated with a sieve size 200 (75 μm) and inspected for microfossils and spherules under the binocular microscope. The spherules were first noted due to their highly spherical shapes and their metallic lustres. Heavy liquid and magnetic separations were used to recover spherules and greatly improved the yield. The surface texture of the spherules was imaged using a SEM Hitachi S-4800 at the Advanced Microscopy Facility of the University of Victoria, operated with a beam current of 10 nA, at an accelerating voltage of 1 kV. The elemental compositions of the spherules were determined using a Bruker EDX detector by analysis of the unpolished surface. The effects of surface geometry make analyses necessarily semi-quantitative; however, EDX spectra can be used to distinguish metal and oxides by the presence of the O Kα peak. Analytical totals for oxide spheres suggest analytical uncertainties of ~10%. Spherules were also imaged by SEM Σigma at the Laboratory of Electron Microscopy and X Ray Analysis of the Universidad Nacional de Córdoba, operated with a beam current of 10 nA, at an accelerating voltage of 5 kV.

5. LOCAL STRATIGRAPHY AND SAMPLING

In the Zenta Range of Cordillera Oriental (Central Andean Basin), the Santa Rosita Formation is represented by a thick succession (~3000 m) consisting of monotonous alternating series of shales and sandstones with subordinate calcareous concretions, coquinas and calcarenites (Figure 3). In 2007, Albanesi collected six calcarenite/coquina samples (total rock weight: 23 kg) to conduct micropalaeontological studies in this area (Albanesi *et al.*, 2011). The micrometeorite-bearing samples were recovered from two distant localities along the road from the Zenta path to the Santa Ana path, in both flanks of a local anticlinal structure (Figure 1 and Table 1). Contamination by artificial spherules in the laboratory can be discounted, since although several samples were processed simultaneously, only three yielded

Table 1. Spherule contents in rock samples from the Precordillera and the Zenta Range

Sample	Latitude (S)	Longitude (W)	Formation	Weight (kg)	Spherules/kg	Biozone	Age (Ma)
Zenta Range							
Z2	23.302	65.018	Santa Rosita	7.45	-	*Acodus deltatus–Paroistodus proteus*	~478-483
Z4	23.354	64.974	Santa Rosita	2.16	78.7	*Acodus deltatus–Paroistodus proteus*	~478–483
Z5	23.354	64.974	Santa Rosita	2.60	-	-	~478–483
Z6	23.357	64.976	Santa Rosita	4.10	-	-	~478–483
Z7	23.336	65.007	Santa Rosita	4.90	0.2	-	~478–483
Z8	23.321	65.006	Santa Rosita	1.40	37.1	*Hunnegraptus copiosus*	~478–483
Precordillera							
LAF24	30.304	68.822	Las Aguaditas	1.16	6.0	*Pygodus serra*	~463–461
LAF30	30.304	68.822	Las Aguaditas	2.45	1.2	*Pygodus anserinus*	~461–459
LAF70	30.304	68.822	Las Aguaditas	3.00	0.3	*Pygodus anserinus*	~461–459
LVacCl	29.696	68.666	La Vacas	1.60	0.6	*Oepikodus evae*	~475–472
Vill1	31.220	68.492	Gualcamayo	0.70	7.1	*Lenodus variabilis–Eoplacognathus suecicus*	~467–464

magnetic spherules. Sample Z4 (78.7 spherules kg^{-1}) was taken from a mudstone level located in the eastern flank of the anticline at Santa Ana path, 15 m below sample Z5, a calcareous coquina that yielded conodonts of the *Acodus deltatus–Paroistodus proteus* Zone of late Tremodocian age, and close to a shaly interval characterized by the graptolite *Araneograptus murrayi* (J. Hall). Sample Z8 (37.1 spherules kg^{-1}) is a silicified greenish-grey fine-grained sandstone with dark brown, slightly calcareous concretions, recovered from the western flank of the anticline at *ca.* 4000 m altitude. Despite the stratigraphic correlation between the aforementioned samples is precluded by the complex tectonics, it is possible to estimate a thickness of about 500 m between samples Z4 and Z8. It yielded an anomalous monospecific concentration of graptolites of the *Hunnegraptus copiosus* Zone; i.e. late Tremadocian (~480 Ma, Albanesi *et al*., 2011). The graptolites are frequently orientated, fragmented and accumulated in large numbers associated with lingulid brachiopods, suggesting mass mortality and bottom reworking by erosive episodes within the basin.

Of the tens of insoluble residue samples that were preliminary inspected for metallic microspherules from different localities of the Precordillera (Figure 1), only four limestone samples yielded positive results (Figure 3 and Table 1). The samples from the Precordillera were exploratory and were selected by their spherule abundance, therefore precluding statistical estimations. The variable number of spherules recovered in each sample may reflect changes in the lithology, depositional environment, bioturbation or in the primary infall rate. Due to the relatively slow deposition and their limited clastic input, the Gualcamayo Formation is optimal for the search of fossil micrometeorites. Sample Vill1 (7.1 spherules kg^{-1}) is a condensed black mudstone, recovered from the basal interval of the Gualcamayo Formation at Don Braulio Creek, where a transitional package of parted limestones covers the San Juan Formation and marks the drowning of the Precordillera carbonate platform (Peralta, 2003). In this section, the Gualcamayo Formation is 39 m thick and extends from the *Lenodus variabilis* Zone to the *Eoplacognathus suecicus* Zone of Darriwilian age (~467–464 Ma) (Sarmiento, 1985; Albanesi and Ortega, 2002). Additionally, three deep-water mudstone samples, LAF 24 (6.0 spherules kg^{-1}), LAF30 (1.2 spherules kg^{-1}) and LAF70 (0.3 spherules kg^{-1}) from the Las Aguaditas Formation, taken at 62, 70 and 116 m, respectively, from its base at the homonymous creek in the Central Precordillera, contained metallic spherules and conodonts referable to the *Pygodus serra* and *P. anserinus* biozones of late Darriwilian age (~463–459 Ma) (unpublished data of Albanesi, cf. Eberlein, 1990). The lower Las Aguaditas Formation correlates to the north with conglomerates of the Las Vacas Formation in the Guandacol area (Albanesi *et al*., 1999). A reworked limestone clast (sample LVacCl, 0.6 spherules kg^{-1}) from the latter stratigraphic unit at Las Vacas Creek yielded one spherule and conodonts referable to the *Oepikodus evae* Zone of Floian age (~475–472 Ma), suggesting erosion and reworking of the San Juan Formation (cf. Voldman *et al*., 2009).

6. RESULTS

A total of ~220 spherules, generally ranging ~75–250 μm in diameter, were recovered from the samples Z4 and Z8 from the Zenta Range of the Eastern Cordillera. Additionally, 17 spherules were obtained from samples from the Argentine Precordillera (Gualcamayo, Las Aguaditas and Las Vacas formations). In the delicate stub mounting process, three of the five magnetic microspherules from the sample Vill1 were lost. The size range of the spherules is consistent with most of the material collected from Antarctica and the deep sea (e.g. Taylor *et al*., 1998; Rochette *et al*., 2008; Parashar *et al*., 2010) and the modern-day extraterrestrial dust flux, which has a mass flux peak at 200 μm (Love and Brownlee, 1993). SEM imaging of the particles reveal hollow, massive, spherical or drop-shaped forms (Figures 4–6). These morphologies are consistent with solidification of a melt droplet since their shapes are in agreement with surface tension. The hollow interior of some spherules is recognized amongst spherules from modern collections and suggested to form by contraction on crystallization (Marfaing *et al*., 2008). Some holes are visible suggesting escape structures of an immiscible phase, such as FeNi metal (Figures 4A, 5E, and 6C).

Most of the spherules exhibit a well-developed crystalline texture of dendrites, also observed in deep-sea spherules. Regularly, polygonal and brickwork textures of equant crystals are also observed (Figure 4C, D) and are similar to Antarctic particles (e.g. Genge *et al*., 1997). The surface textures have been described by numerous authors (Koeberl and Hagen, 1989; Wang and Chatterton, 1993; Yada *et al*., 1996; Szöőr *et al*., 2001; Stankowski *et al*., 2006; Dredge *et al*., 2010; Korchagin *et al*., 2010), and are related to rapid cooling from high temperatures precluding a sedimentary or diagenetic origin for the spheres. EDX analysis of the particles suggests they are composed principally of low-Ni, iron oxides consistent with I-type spherules (Table 2), containing mainly magnetite and/or wüstite with rare Fe-Ni metal droplets (Genge *et al*., 2008). Wüstite is metastable at low temperatures, being extremely rare in terrestrial rocks, but present in the fusion crusts of iron meteorites. The occurrence of metallic iron among the analysed microparticles also supports their cosmic origin (see spherule Z8-8 in Table 2), as native metal is exceedingly rare in terrestrial volcanic rocks due to their higher oxygen fugacities. Surface EDX indicates up to ~1 wt% Al, Si, Ca, Mg, Ni, Co and Cr.

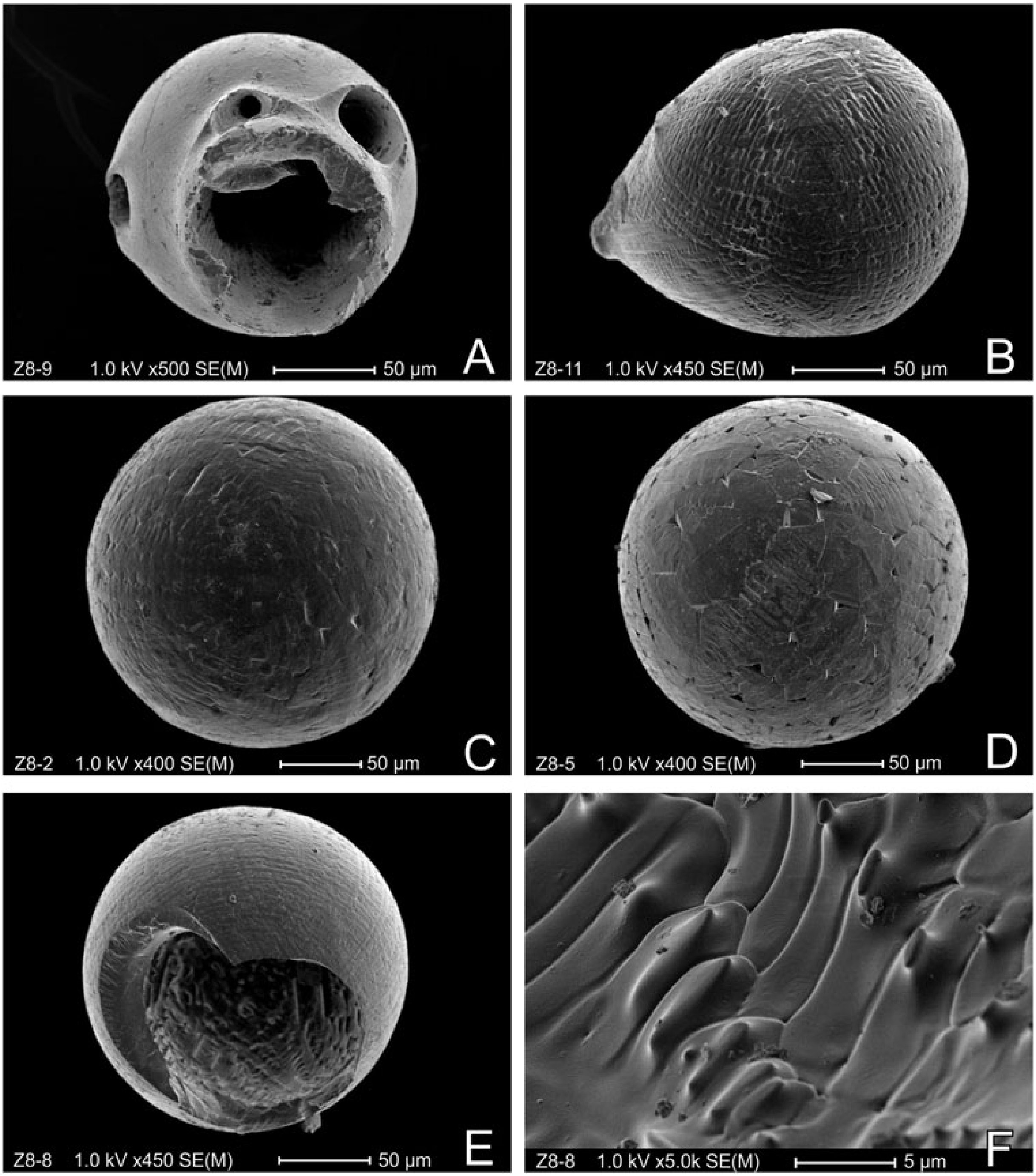

Figure 4. SEM secondary images of I-type spherules from the Santa Rosita Formation (late Tremadocian) recovered from the Zenta Range in Cordillera Oriental. (**A**) Spherule with dendritic texture and extreme distortion due to outgassing structures. (**B**) Drop-like spherule with polygonal texture and protruding knobs. (**C**) Spherule with coarse polygonal texture. (**D**) Spherule showing brick-work texture superposed on a polygonal pattern. (**E**) Hollow spherule displaying dendritic texture. (**F**) Detail of the inner side of spherule E showing a fine dendritic pattern.

7. INTERPRETATION

Spherical particle morphologies are particularly ambiguous since they may be terrestrial (e.g. diagenetic, biogenic, volcanic, anthropogenic), extraterrestrial or may be delivered from the impacts of crater-producing meteorites, as dissipated melt (Raukas, 2000; French and Koeberl, 2010). Although Ni enrichment is usually considered a marker for an extraterrestrial origin, only minor amounts of Ni were detected in the spherules (Table 2). This is in accordance with the heating of

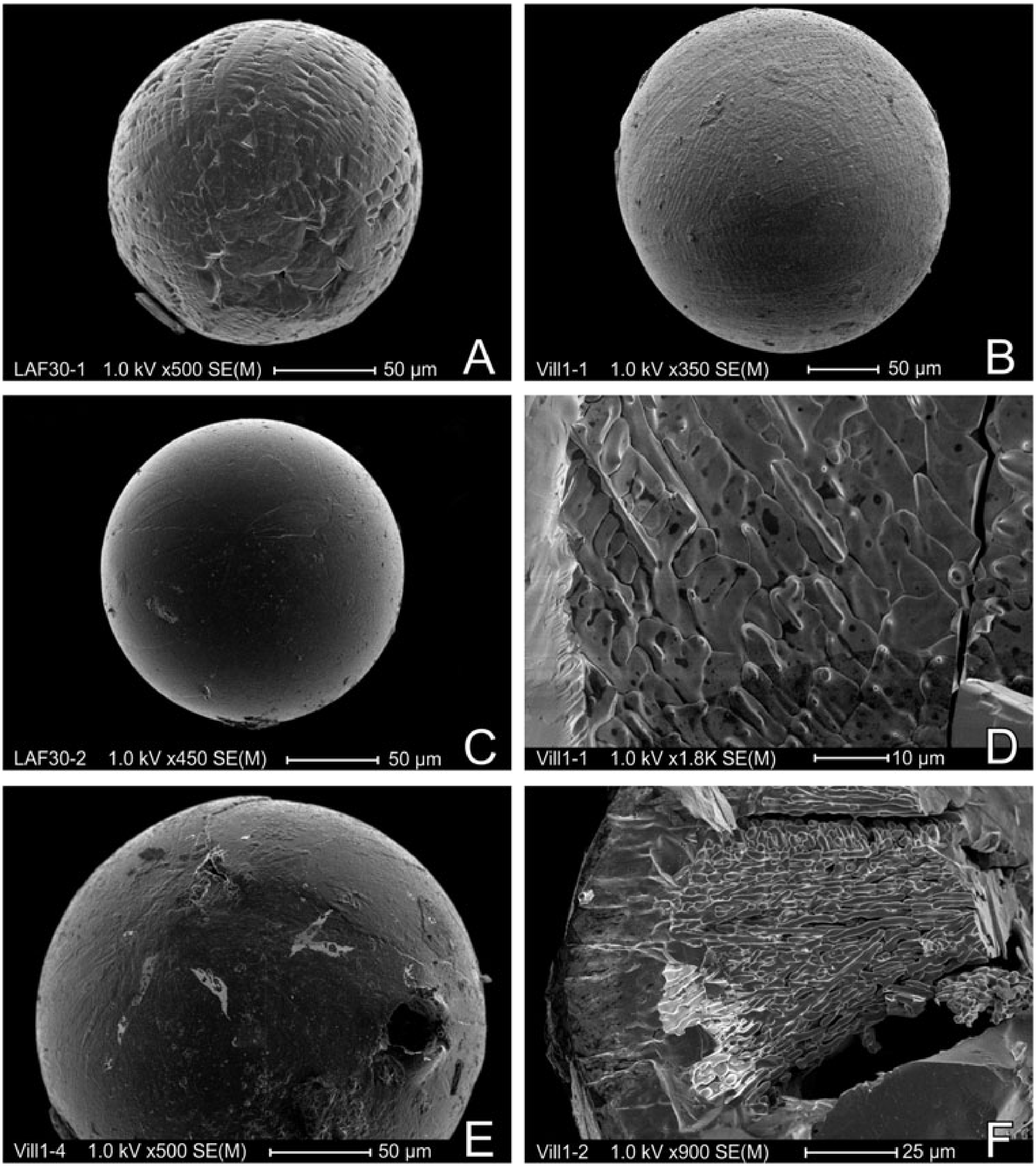

Figure 5. SEM secondary images of I-type spherules recovered from the Precordillera. The variable features of these particles suggest quite different thermal histories (cf. Marini *et al*., 2004). For the sample location and age refer to the text. (**A**) Spherule with coarse polygonal pattern. (**B**) Spherule with fine dendritic pattern (filigree). (**C**) Spherule with distinctive smooth surface. (**D**) Detail of the inner side of the spherule B showing a hollow core with a fine dendritic pattern. (**E**) Spherule with smooth surface, minor cracks and escape structure. (**F**) Inner side of a spherule showing a fine dendritic pattern surrounded by thick, massive walls.

I-type spherules during atmospheric entry: as the micrometeorites melt to form immiscible silicate/oxide and metallic melts, these are subsequently separated into individual spherules due to density contrast during deceleration (Brownlee *et al*., 1984). A significant proportion of the metallic liquid oxidizes during entry heating, leaving a high Ni metallic core, very occasionally with a Pt group-rich nugget. Depending on the deceleration experienced, metallic cores of the spherules migrate to the front of the particle and separate, leaving a remnant that comprises a Fe-oxide spherule free of Ni (Bi *et al*.,

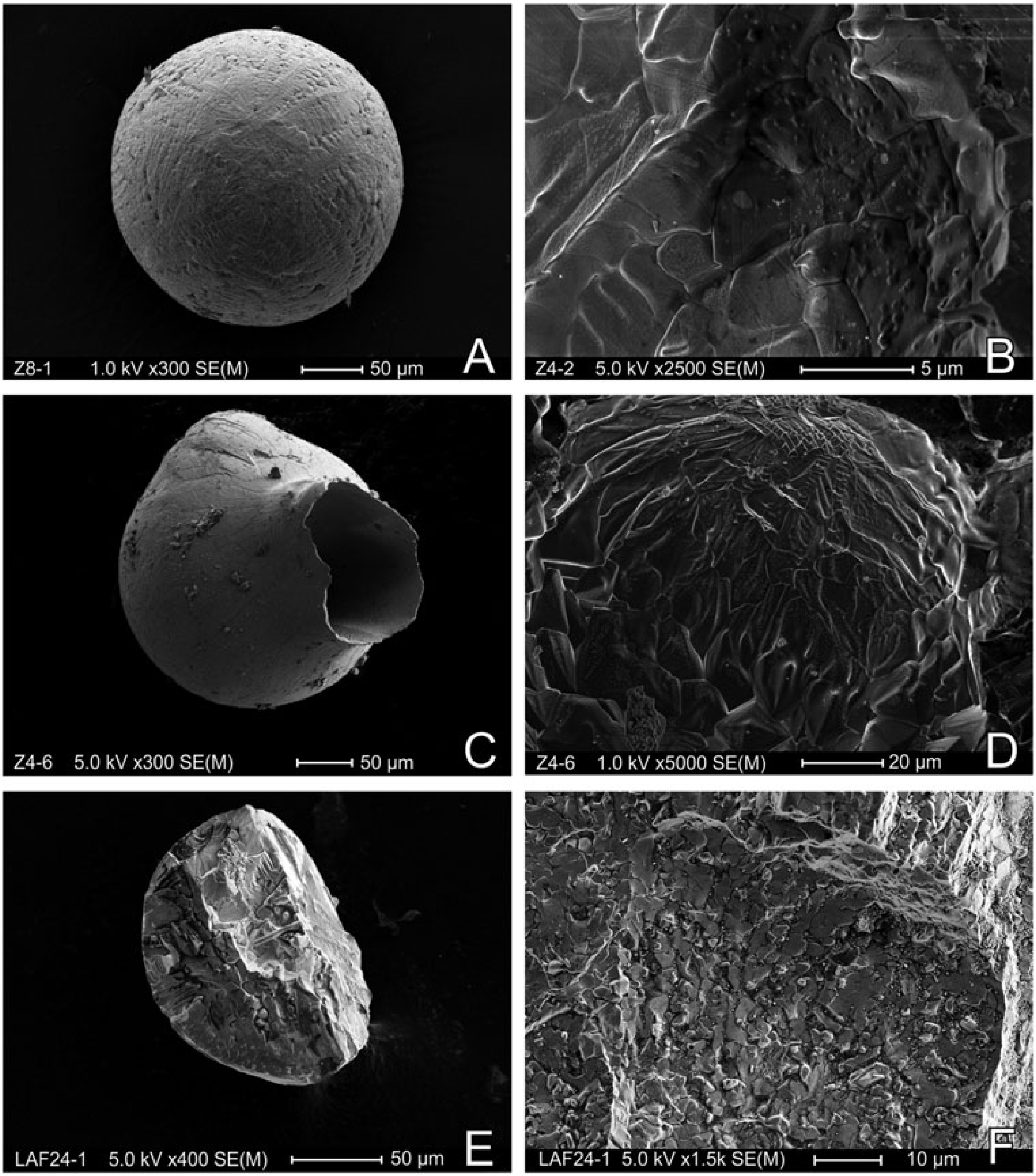

Figure 6. SEM secondary images of I-type spherules recovered from the Precordillera (sample LAF24-1) and the Zenta Range (samples Z4 and Z8) in Cordillera Oriental. (**A**) Spherule with fine polygonal pattern. (**B**) Detail of the inner side of a spherule showing a hollow core with a fine dendritic pattern. (**C**) Spherule with smooth texture and extreme escape structure. (**D**) Similar to B. (**E–F**) Broken hollow spherule showing an inner fine dendritic pattern.

1993; Yada *et al.*, 1996). Similar I-type spherules depleted in Ni occur in Ordovician rocks of the Durness Group in NW Scotland (Dredge *et al.*, 2010), in Oligocene sediments in the coastal plain of South Carolina, USA (Taylor *et al.*, 1996), and in modern collections from the Transantarctic Mountains (Rochette *et al.*, 2009) and the Central Indian Ocean (Parashar *et al.*, 2010). Conversely, droplets produced during meteorite ablation form at lower altitudes and contain higher Ni concentrations, in response to the higher oxygen fugacity (Genge and Grady, 1999). Products of Tunguska-like disruptions of larger bodies are likewise Ni-bearing due to their low terminal altitudes (van Ginneken *et al.*, 2010).

Table 2. Chemical composition of the spherules by surface EDX analysis (unpolished samples)

Component	LVacCl-1	LAF30-1	LAF30-2	LAF70-1	Vill1-1	Vill1-2*	Vill1-4	Z8-3	Z8-8
O	24.37	19.93	16.20	19.10	14.70	19.67	18.59	26.56	0.03
Fe	72.67	77.85	81.59	77.19	82.77	77.22	77.60	69.00	95.98
Ni	0.00	0.00	0.02	0.10	0.00	0.09	0.06	0.01	0.00
Co	0.96	1.00	1.00	1.03	1.06	1.16	1.00	0.98	2.66
Al	0.37	0.14	0.04	0.72	0.36	0.50	0.50	0.00	0.00
Si	0.34	0.20	0.07	0.13	0.06	0.00	0.36	0.21	0.00
Ti	0.02	0.03	0.00	0.00	0.10	0.00	0.03	0.00	0.00
Cr	0.05	0.05	0.16	0.17	0.14	0.16	0.17	0.03	0.11
Ca	0.08	0.04	0.03	0.04	0.04	0.03	0.06	0.03	0.07
Mg	0.15	0.07	0.08	0.08	0.04	0.05	0.14	0.12	0.00
Others	0.99	0.69	0.81	1.44	0.73	1.12	1.49	3.06	1.15

Unit of measure of chemical components: wt%.
*Measured on the inner side of the particle.

Spherules produced by collisions of larger objects that generate impact craters have a range of compositions relating to mixtures of melted and vapourized target rocks and projectile materials. Those microtektites incorporating significant materials from projectiles can include iron oxides, of which Ni-rich spinels are important tracers of meteorite impacts due to their formation in atmosphere at high fO_2 (e.g. Robin and Molina, 2006).

Silicate and glass spherules were not observed during the picking procedure, perhaps as a result of the magnetic technique used for extraction. Alternatively, this could be explained by preferential weathering, dissolution and destruction of the S-type particles in deep-sea deposits with increasing depositional age, as suggested by Onoue *et al.* (2011), to account for an anomalously small proportion of S-type spherules (3%) and a large proportion of I-type spherules (94%) in an Anisian (~240 Ma) chert from Japan.

Iron-rich industrial spherules are very common in the terrestrial environment and can appear similar to the proposed micrometeorites. However, magnetic spherules of industrial origin (e.g. coal-fired power plants, welding operations) usually exhibit perfectly spherical shapes with smooth, polished surfaces, and may have grains of zircon and other minerals welded upon them (e.g. see Puffer *et al.*, 1980; Blaha *et al.*, 2008; Uścinowicz, 2009). Typical contamination fly-ash spherules are comparatively poor in Fe but rich in Si, Al, and minor admixtures of other elements (Na, Ca, Mg, K) (Marvin and Einaudi, 1967; Shoumkova, 2011).

Contamination is more likely in the case of samples recovered from recent ice/sediments and not from outcrop rocks. Anthropogenic contamination can be discounted since the samples were washed with water and the spherules occur diagenetically attached to the host sediment. Additionally, industrial and volcanogenic magnetic spherules tend to be rich (~5%–10%) in Ti (Szöőr *et al.*, 2001; Korchagin *et al.*, 2010), whereas it only constitutes a trace component in the current particles. Volcanic magnetites are never pure, but rather, titaniferous or, in volcanic sublimates, display Ni and Cr substitutions (El Goresy, 1968; Toutain *et al.*, 1985). According to del Monte *et al.* (1975), volcanic ferromagnetic particles are also characterized by crystals generally idiomorphic, mostly octahedron and rhombic dodecahedron shapes, and by the absence of hollows (cf. Miono, 1995). Additionally, Wright and Hodge (1965) observed that metallic microspherules are extremely rare in volcanic ash deposits sampled in volcanic areas, in contrast to the ferromagnetic matter found in Arctic and Antarctic ice. Otherwise, thermodynamic considerations, the morphology, and the absence of magmatic silicate inclusions rule out a volcanogenic genesis for our spherules (del Monte *et al.*, 1975; Iyer *et al.*, 1999).

A biogenic origin for the spherules can be rejected by the presence of dendritic structures within the particles. This type of structure is due to quenching under rapid cooling of molten material at high temperature. Alternatively, Suk *et al.* (1990) demonstrated that magnetite spheres may originate by alteration of framboidal pyrite. However, the structures observed in our spherules do not agree with framboidal pyrite precursors.

In summary, the internal and external microstructural features, and the chemical and mineral compositions all strongly favour an extraterrestrial origin for our metallic microspherules.

8. DISCUSSION AND CONCLUSIONS

Fossil cosmic microspherules provide insights into the fluctuation of accretion rates of extraterrestrial matter to Earth, variations in the composition of the flux, and the influence of these processes on climate change and the evolution of life on Earth. I-type cosmic spherules are abundant in deep-sea collections, as they have greater resistance to weathering under sea-water in contrast to the silicate and glassy spherules. However, they constitute only 1%–3% in the Antarctic micrometeorite collections, a value similar to the ~5% found for iron meteorite falls (e.g. Rochette *et al*., 2008). From the study of the South Pole Water Well micrometeorite collection (Taylor *et al*., 2000), we estimate a current flux rate of I-type spherules $>100\,\mu m$ of $3.4\times10^{3}\,Ma^{-1}\,m^{-2}$ (recalculated from Rochette *et al*., 2008).

The late Tremadocian samples Z4 and Z8 from Cordillera Oriental contain 78.7 and 37.1, respectively, spherules per rock kilogram (Table 1). Assuming a sandstone density of $2500\,kg\,m^{-3}$ for the samples, this is equivalent to $\sim 9.2–19.6\times10^{4}$ spherules m^{-3} of rock. Given the structural complexity and the lack of detailed fossil records, it is difficult to assess the sedimentary deposition rate of the Santa Rosita Formation in the study area. As a preliminary estimate, and considering an integrated stratigraphic column of the basin (Buatois *et al*., 2006), the sedimentary deposition rate of the Santa Rosita Formation (upper Furongian–Tremadocian) is $\sim 100\,m\,Ma^{-1}$. Thus, the mean spherule accumulation rate is $\sim 9.2–19.6\times10^{6}\,Ma^{-1}\,m^{-2}$.

This preliminary estimate is consistent with the period of elevated flux of extraterrestrial material, as recorded several thousand kilometres apart in Scotland, Sweden and central China, and the high abundance of Middle to early Late Ordovician craters discovered in Laurentia and Baltica (Figures 2 and 3) (Schmitz *et al*., 2001; Alwmark *et al*., 2010; Cronholm and Schmitz, 2010; Dredge *et al*., 2010; Earth Impact Database, 2011). The wide differences in cosmic spherule contents, both between the two Argentinean basins and the previous Ordovician flux estimations from the above authors, may arise from uncertainties in the sedimentary rate estimates, which are critical in all flux calculations. In particular, the greater spherule abundance in the clastic sedimentary rocks from Cordillera Oriental could reflect local processes, such as redistribution of spherules by ocean-floor currents. This is supported by the anomalous concentration of orientated graptolites, which accumulated concurrently with lingulids (Albanesi *et al*., 2011). Moreover, the estimated accumulation rate value must be considered as highly speculative, since the time-span needed for sedimentation of one sedimentary bed is unconstrained and it does not consider periods of erosion or the sampling of anomalously-rich spherule layers. Interestingly, these layers deposited before the L-chondrite body breakup (~470 Ma) and yet they contain a much larger content of spherules than do the younger Precordilleran samples. A fully integrated stratigraphic and biostratigraphic approach is required to obtain a reliable sedimentation rate for the Santa Rosita Formation at the Zenta Range and to confirm the temporal variations in the flux of extraterrestrial matter during its deposition.

On the other hand, the size range of our cosmic spherules is 75–250 µm, in agreement with most populations reported from modern samples (e.g. Taylor *et al*., 2000). Size comparison with correlative cosmic spherules from Scotland (Dredge *et al*., 2010) is precluded by the different sieves employed for extraction. Nonetheless, they show similar mineral and major element compositions, containing trace levels of Al, Si, O, Ti, Mg, Ca and Cr, and typical dendroidal structures.

Parnell (2009) related the enhanced Middle Ordovician meteorite flux with global-scale deposition of olistostromes by destabilization of continental margins following meteorite impacts. The author proposed that up to 500 impactors of 100 m in diameter, including 250 impactors if only landward impacts are considered, fell within about 30 km of the 20 000-km-long Iapetus coastline. Alternatively, Meinhold *et al*. (2011) challenged the idea that mass wasting was mainly produced by meteorite impacts over a period of almost 10 Ma, and proposed an earthquake-driven mechanism related to plate-tectonic processes, possibly magnified during a period of global sea-level lowstand.

The particles recovered in the current study are I-type spherules which represent only a small fraction of the current-day micrometeorite flux and are formed from extraterrestrial dust, rather than large objects such as meteorites (Genge *et al*., 2008). The iron-oxide dominated nature of these spherules suggests that their pre-atmospheric precursors were FeNi metal grains. Metal does occur within L-chondrites at abundances of around 1 vol%. The observed spherules could, therefore, be related to the L-chondrite break-up event.

An elevated extraterrestrial dust flux does not necessarily imply that large impacts occurred at this time, since the large numbers of dust particles derived from disruption of the L-chondrite parent body are much more likely to be captured by the Earth than the relatively small numbers of objects >500 m in size produced by the event. Indeed, the absence of Ni-rich spinels amongst particles recovered in this study implies a lack of detectable impact ejecta in the horizons sampled.

Impact, extraterrestrial and volcanic spherules are increasingly used for geological correlation. The apparent absence of cosmic spherule enrichments in the limestones and condensed shales from the Precordillera, in contrast to the Cordillera Oriental levels, could reflect uncertainties in sedimentation rate or sedimentological controls on spherule accumulation and survival, due to concentration of ‘heavy mineral’ spherules due to transport. Indeed, this study reveals that not all sediments are created equally when it comes to their spherule contents. Whether the I-type spherules reported here are part of the L-chondrite influx remains uncertain, in particular, due to the lack of chromites that are frequently considered a unique component of the mid-Ordovician 'spike' from the breakup of the L-chondrite body at *ca*. 470 Ma (e.g. see Alwmark and Schmitz, 2009). Future geochemical, petrographical and biostratigraphical studies, with targeted searches for spherules, would provide evidence of the true magnitude and geographical distribution of these cosmic events during the early Phanerozoic history of the Earth and its role during the explosion of biodiversity in the Ordovician Period (e.g. Schmitz *et al*., 2008).

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