The Valdemiedes Event: Mineralogical and Geochemical Insights for a Global Lower-Middle Cambrian Event

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INTRODUCTION.

The Cambrian Series 2 and Series 3 (formerly Lower-Middle Cambrian) boundary event is one of the strongest Phanerozoic faunal turnovers. This global event, called in Spain the Valdemiedes Event, caused a noticeable extinction of trilobites as well as an almost complete extermination of other Early Cambrian marine animals, such as archaeocyaths.

The stratigraphic division and correlation of the Lower/Middle Cambrian boundary is a global problem that has not yet been perfectly solved and continues as the focus as major discussions. One of the important causes is the existence of two global biogeographic regions during the period from Early Cambrian to Middle Cambrian: Indian-Pacific and Atlantic regions. Much work has been done and great achievements have been acquired in this aspect, since the fauna disappearance has been considered as contemporaneous global perturbations instead of diachronous regional events.

For the above reasons, some researchers began to look for other methods of stratigraphic division, for example, the geochemical methods. Among the geochemical methods, those using isotopic signatures are the best, and a great progress has been made in the chemostratigraphic division of Lower/Middle Cambrian boundary. The typical studies in this aspect involve carbon and strontium isotopes in the strata at the Lower/Middle Cambrian boundaries in Siberia and North America. The results revealed noticeable $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ excursions near the Lower/Middle Cambrian boundaries. These results are generally consistent with boundaries divided on the basis on trilobites and acritarchs.

The Lower/Middle Cambrian boundary at Rambla de Valdemiedes section (Murero, Zaragoza province) has been well documented from a palaeontological point of view (Liñan et al., 2006 and references therein). The goal of this contribution is to carry out a geochemical investigation to facilitate global stratigraphic correlation.

RAMBLA DE VALDEMIEDES (RV2) SECTION.

The Rambla de Valdemiedes (RV2) section is located 2 km northwest to the Murero village (Zaragoza Province, NE Spain), in the heart of the Cadenas Ibéricas. This section is one of the Global Stratotype Section and Boundary Point (GSSP) proposed for Series 2/3.

The Cadenas Ibéricas is a Hercynian-Alpine range peripheral to the Iberian Massif. The affiliation of Cambrian rocks of Cadenas Ibéricas to Lotze's (1961) tectonostratigraphic zones was further developed by Gozalo & Liñán (1988): the Cadena Ibérica Occidental (where Murero is located) belongs to the West Asturian-Leonese zone.

The studied segment of the RV2 section is a 75 m-thick, monofacies succession of shales with some carbonate nodules and minor marly shales, white claystone and discontinues greenish-grey fine-grained sandstone interbeds. All the above materials contain a number of exceptionally preserved fossils (Lagerstätten); including trilobites, echinoderms, brachiopods, sponges and Burgess Shale-type fossils. Palaeoecological conditions evolved upsection from restricted to more open subtidal.

MINERALOGY AND CHEMOSTRATIGRAPHY.

The samples and their 20-2μm and <2μm fractions were characterized by X-Ray Diffraction (XRD). Powdered samples were weighed, placed in tin capsules and put in a rotating carrousel for combustion in an elemental analyser. The gas sample was subsequent purified and passed through an ISOPRIME continuous flow dual-inlet mass-spectrometer for isotopic analysis. The results are expressed in the notation d in relation to PDB scale. Those samples containing carbonates were pre-treated following the Larson et al. (2008) method.

Knowledge of the phyllosilicate association and its crystallochemical parameters allows one to monitor post-depositional evolution of the rocks. Taking into account that organic matter is pretty sensitive to such an evolution, our mineralogical study was designed to address the extent to which post-depositional evolution may alter the original isotopic ratios recorded by the studied samples and consequently to evaluate its influence on further interpretations.

The bulk mineralogy comprises quartz, mica, and chlorite as the main components and feldspar as accessory one. Occasionally, calcite and dolomite have been detected as a rare component in the Valdemiedes sections. In fine fractions, the main phases are muscovite and chlorite. The mica crystallinite (IC) values range from 0.25 to 0.30 º2θ (mean value = 0.29º2θ). These values are consistent to those reported by Bauluz et al. (1998) for Cambrian terrigenous sedimentary sequence of the Cadenas Ibéricas and are indicative of an anchizone grade. No evolutionary trend has been observed at local or regional scales either in silt or clay fractions.

Plotting $\delta^{13}C_{org}$ versus stratigraphic height for RV2 section reveals an architecture consisting of $\delta^{13}C_{org}$ values

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reach lighter value of -31.5‰ at 7a stratum corresponding to Valdemiedes Event and "background values" below and above this peak between -27,0 and -20,9 ‰. The portion of the sequence below the negative peak is marked by the fluctuation of the $\delta^{13}C_{org}$ values between -24.6 to -16.0 ‰. From the negative shift up, carbon isotopic values increase to the aforementioned baseline (values range from -28.4 to -24,6‰). By contrast, $\delta^{13}C_{org}$ values do not fluctuate back and forth in the way showed at the bottom of the section.

Since post-depositional alteration is of particular concern when constructing an isotopic profile, pertinent to our discussion is to consider post-depositional effects on primary $\delta^{13}C_{org}$ values, taking into account the low carbon concentrations in the studied samples (x=0.09%, n=29). As already said, data accumulated by Bauluz et al. (1998) and ourselves have show that all the Cambrian terrigenous sediments have undergone a post-depositional evolution what promoted organic matter alteration, showing an evolutionary trend to heavier values. Therefore, absolute values must be regarded with caution. Nevertheless, the presence of a negative $\delta^{13}C_{org}$ shift, which correlates with that reported through the Lower/Middle Cambrian over the same stratigraphic interval in sections from different places over the world and that the fact that there is no post-depositional alteration gradient throughout the studied sections, indicate that the isotopic data are recording changes at global scale (Guo et al., 2010).

THE VALDEMIEDES EVENT.

Both palaeontological and geochemical markers define the Valdemiedes Event. In our case study, the negative $\delta^{13}C_{org}$ excursion can be correlated with the appearance of the *Acadoparadoxides mureroensis* FAD (First Appearance Datum) in the Rambla de Valdemiedes (RV2 and RV1) sections. This polymeroid trilobite species is widely distributed across one palaeocontinent at least, namely Western Gondwana (Spain, Morocco, Italy, Turkey) and is recorded also in Siberia and probably Poland, and its FAD has been accurately correlated with the main Cambrian successions of the world (Gozalo et al., 2007). Besides, the appearance of paradoxidids has been considered as the beginning of the former middle Cambrian Series in Europe, Africa, eastern North America, and Russia. Consequently, the negative carbon isotopic excursion at the Valdemiedes section allows us to make chemostratigraphic correlations with other biogeographic regions at Cambrian times since the appearance of strongly negative carbon isotopic excursion at the lower/middle Cambrian boundary is a ubiquitous worldwide phenomenon.

The negative $\delta^{13}C_{org}$ excursion is considered to have been caused by: (i) the introduction of $\delta^{13}C$-depleted, anoxic water into shallow-water carbonate platforms during the latest Early Cambrian transgression, and (ii) the associated decrease in organic carbon burial amount due to the major biomass reduction. An anoxic water column below the surface mixed layer may have prevailed in Early Cambrian oceans during the transgression, accompanied by the sluggish circulation and strong stratification. These oceanic conditions would be favoured by the low-latitude continentality that typically marked the Early Cambrian greenhouse period.

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