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The Upper Devonian Kellwasser Event recorded in a regressive sequence from inner shelf to lagoonal pond, Catalan Coastal Ranges, Spain

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ABSTRACT

This study, conducted in the Catalan Coastal Ranges, north-east Spain, describes the Upper Devonian Kellwasser event in a shallowing-upward sequence of black shales, siltstones and quartz arenites. This sequence was deposited in a progradational and regressive coastal system where the sedimentary environment evolved from the inner shelf to a lagoonal pond located landward of the shoreline. Three anomalous succeeding steps have been identified by geochemical analysis. The first one, detected on the inner shelf, was characterized by oxygen depletion and high organic productivity. The second, detected in the nearshore, was caused by hydrothermal activity occurring under normal oxic conditions. The third and most intense step was identified in the muds of the lagoonal pond and has been linked to strong anoxic conditions, elevated clastic input derived from changes in the weathering regime at

the source area and moderate hydrothermal activity. The Kellwasser event is thus defined in the study area as stepwise and multi-causal. This is the first time that the Kellwasser event has been identified in a sedimentary environment behind the shoreline. It is also the first time that it has been reported in the Catalan Coastal Ranges.

Keywords Anoxia, Catalan Coastal Ranges, environmental stress, Frasnian–Famennian boundary, Kellwasser event, lagoonal pond.

INTRODUCTION

Global anoxic events result in biotic crises that represent turning points in the evolutionary history of the Earth (Hart, 1996; Hallam & Wignall, 1997; Erwing 2001). The deposits most commonly associated with such events consist of organic-rich mud layers deposited in highly reducing marine environments. Their analysis is of interest because they are not only essential in the understanding and recovery of biologically stressed environments but are also precursors of natural resources, such as ore deposits or fossil fuels (Demaison & Moore, 1981; Calvert, 1990; Grauch & Huyck, 1990; Potter *et al.*, 2005; González *et al.*, 2006; Lehmann *et al.*, 2007; Piper & Calvert, 2009; Bjorlykke, 2015; Slack *et al.*, 2015).

The Devonian was an outstanding time for the occurrence of local/global events (both anoxic and non-anoxic) and environmental crises because, in addition to the most common reasons that have been proposed to explain such episodes, the expansion of terrestrial plants produced severe environmental modifications (Retallack, 1997; Algeo & Scheckler, 1998; Algeo *et al.*, 2001; Copper, 2002; McGhee, 2013). As a result, the entire Devonian system is scattered with events and crises, but those with the greatest environmental and biological impact occurred during the Late Devonian (McGhee, 1996; Walliser, 1996). Among these, are the Frasnian–Famennian Kellwasser and the Devonian–Carboniferous Hangelberg anoxic events, which have received much attention because they are associated with stage or system boundaries (Denayer & Mottequin, 2015). Both of these events are the

most critical ones, not in terms of number of extinct species but in purely ecological terms (Joachimski & Buggisch, 1993; House, 2002; Racki, 2005; Carmichael *et al.*, 2014, 2016; Stanley, 2016).

The Kellwasser, initially conceived as a mass extinction event, has been classified more recently as a mass depletion diversity episode (Bambach *et al.*, 2004). Formerly defined in Germany by Buggisch (1972), it has traditionally considered to be one of the 'Big Five' biodiversity crises (Raup & Sepkoski, 1982), occupying the fourth position in the ecological severity rank defined by McGhee *et al.* (2004, 2013). Considered to be an important evolutionary bottleneck (Sandberg *et al.*, 1988; Copper, 2002; House, 2002; McGhee *et al.*, 2004; Bond, 2006; Sallan & Coates, 2010; Stignall, 2012), the Kellwasser event has been extensively studied from a palaeontological perspective, as it is largely used for global correlations all over the world. Most available literature on the Kellwasser event focuses on sequences deposited on platforms, slopes or marine basins. In contrast, studies focused on littoral environments are rare; to date, there is no record of the event in emerged depositional environments apart from erosive surfaces (Ettensohn, 1994; Schieber, 1998, Piecha, 2002, Rodriguez-Cañero & Martin-Algarra, 2014).

In this study, the Kellwasser event is recorded for the first time in a sedimentary environment behind the shoreline. It depicts a shallowing-upward detrital sequence deposited on a prograding coast that evolved from the inner shelf to a lagoonal pond. Synchronous with deposition, three anomalies of increasing environmental stress were recorded, with the last and most intense located within the swamped mud of the coastal plain. This is also the first time that the Kellwasser event has been reported in the study area, the Catalan Coastal Ranges (CCR).

REGIONAL GEOLOGICAL SETTING

The CCR consists of two narrow and elongated ridges separated by a central depression, all running parallel to the Mediterranean coast of north-east Spain. With a north-east/south-west direction, it extends *ca* 250 km from the southern margin of the Pyrenean Belt to the Ebro Delta (Fig. 1A). The ridges include a Variscan basement mostly made up of sedimentary rocks and upper Permian granitic intrusions unconformably overlain by Mesozoic sedimentary cover. The central graben is filled with Miocene detrital sediments. The current cartographic configuration of the CCR is derived from the former palaeogeography and the double effect of the Variscan and Alpine orogenies in this region (Julivert & Durán, 1990a; Melgarejo, 1992; Ortí, 2004). The location of the CCR within the Iberian Massif, and in a wider context within the European Variscan Belt, is still imprecise, despite its assignment to the West Asturian–Leonese Zone (Navidad *et al.*, 2010). Palaeogeographically, it is considered to occupy an intermediate position between the Montagne Noire in France and the Chenoua Massif in northern Algeria (Julivert & Durán, 1990b; Raymond & Caridroit, 1993).

The Palaeozoic stratigraphic record in the CCR includes Cambrian to Carboniferous units that are unevenly distributed from north to south (Figs 1A and 2). The north is dominated by large outcrops of pre-orogenic Lower Palaeozoic rocks and poorly exposed thin Devonian and Carboniferous successions (syn-orogenic deposits) (Julivert & Martínez, 1983; Julivert & Durán, 1990a). To the south, this trend changes drastically because the Carboniferous rocks outcrop more widely, the Devonian more scarcely and deposits of the Lower Palaeozoic are absent. The distribution of pre-orogenic (to the north) and syn-orogenic (mostly to the south) outcrops in the CCR probably relate to the former palaeogeography of the area (Julivert & Durán, 1990b). In detail (Fig. 2), the Cambrian–Middle Ordovician? series consist of a thick succession of shales, sandstones and minor limestones that have been slightly to intensely metamorphized and segregated in different

units bounded by stratigraphic discontinuities. These units have received local names and are generally imprecisely dated (Melgarejo, 1992; Sanz-López et al., 2000). The Upper Ordovician-Lower Devonian succession is continuous (Julivert and Durán, 1990a, 1992; Sanz-Lopez et al., 2000, among others). At its base, the Upper Ordovician includes conglomerates (Sant Cebrià Formation), volcanic and volcanoclastic rocks (Els Metges Formation), limonitic sandstones and shales (Mas Cals Formation) and grey to black shales intercalated with thin sandstones (Avanco/Fitor formations). The Silurian rocks comprises graptolite shales (Llandovery to lower Ludlow), massive limestones (La Creu Formation, upper Ludlow-Pridoli) and another thin graptolite-rich shale level representing the Silurian-Devonian transition. The Devonian record is poorly exposed. To the north, it includes Lochkovian–lower Pragian shallow marine limestones (Olorda Formation) and a thin informal unit of shale dated as lower Famennian. To the south, it is represented by the Givetian?–Frasnian Les Vilelles unit (Julivert et al., 1985; Julivert & Durán, 1990b; Gutiérrez-Marco et al., 2004), whose uppermost part is the focus of this study (Fig. 2).

Finally, the Carboniferous includes Mississippian rocks exposed throughout the CCR. To the north, it is reduced to three small units, dominated by chert, limestone and sandstones (corresponding to the Aigua-Feda, Papiol and Cánoves formations, respectively), that reach a total thickness of 50 m (Martínez-Chacón et al., 2003). To the south, it consists of a thick pile of turbidites, several thousands of metres thick, that contains a thin level of radiolaritic chert at the base. The entire sequence is divided into three units, namely the Basetes, Scala Dei and Poboleda (Orche & Colodrón, 1977; Orche et al., 1977; Colodrón et al., 1979; Sáez, 1992).

The Les Vilelles unit

The Les Vilelles unit represents the only Devonian rocks recorded in the southern CCR (Fig. 2). Its relationship with the underlying unit is unknown because its base is not exposed. At its top, it is unconformably surmounted by Carboniferous (Tournaisian to early Viséan)

radiolaritic chert and turbiditic deposits (Raymond & Caridroit, 1993). This contact is an erosive to a gently angular first-order unconformity.

Informally described by Sáez (1982), the Les Vilelles unit consists of a monotonous series, greater than 250 m thick, of grey/black shales and centimetre thick sandstone beds originally dated by palynomorphs as Middle–Late Devonian (Colodrón *et al.*, 1979) and interpreted as deep marine deposits (Sáez, 1982; Sáez & Anadón, 1989). The last 20 m of the unit exhibit strong sedimentological disparities and grain-size controlled diagenetic silicification. This upper part of the unit represents the studied section in this paper. It has been named as the FF Les Vilelles section (Fig. 3).

The entire unit crops out at the Priorat Massif, occupying the core of a complex asymmetrical anticline trending at N145E and flanked by detrital Carboniferous rocks (Fig. 1B). In the northern limb, the Devonian and Carboniferous series show depositional relationship, while in the southern limb, the Les Vilelles unit overthrusts the Pennsylvanian series.

A high precision palynostratigraphic study conducted by González *et al.* (2015) in the FF Les Vilelles section (Fig. 3) provided a moderately abundant assemblage of miospores, acritarchs, prasinophyte phycmata and less abundant chitinozoans that was assigned to the latest Frasnian, immediately prior to the Famennian. In detail, the joint occurrence of the miospore species *Teichertospora torquata* (Higgs) McGregor & Playford (1990), *Grandispora gracilis* (Kedo) Streel in Becker *et al.* (1974) and *Diducites mucronatus* (Kedo) emend. Van Veen (1981) supports assigning the studied section to both the upper Frasnian–lower Famennian *torquata-gracilis* assemblage zone of Richardson & McGregor (1986) and the intermediate of the three interval zones subdividing the *Rugospora bricei*–*Cymbosporites acanthaceus* (BA) oppel Zone in the scheme defined by Streel *et al.* (1987). However, the occurrence of the chitinozoan species *Fungochitina pilosa* (Collinson & Scott, 1958) constrains this age to the late Frasnian. This interval corresponds to the uppermost *rhenana*

and *linguiformis* conodont zones defined by Ziegler & Sandberg, 1990 (González *et al.*, 2015, fig. 7).

MATERIALS AND METHODS

The study of the FF Les Vilelles section was conducted in two successive stages. The first stage, which focused on obtaining a better understanding of the regional geology, involved the detailed mapping of the study area and establishing a stratigraphic log. In parallel, a palynostratigraphic analysis of the black shales constrained the age of the upper part of the series (González *et al.*, 2015). The relevance and precision of the age provided and the abundance of dark to black shales resulted in a second sampling program to geochemically characterize the sequence and refine previous sedimentological and palynological analyses.

Primary sedimentological analysis was based on classic fieldwork. The interpretation of processes and depositional environments was based on lithology, thickness, internal ordering, geometry of layers and packages, sand/shale (s/s) ratio, sequential evolution, post-sedimentary structures and palynological record. The facies associations thus defined represent depositional units in pure classical terms. To constrain the spatial-temporal evolution of sedimentary environments, depositional interpretations and analysis of the fluctuation of the continental/marine influence across the stratigraphic column were considered. The petrographic analysis of thin sections using transmitted and reflected light microscopy, image analysis and scanning electron microscopy (SEM) photography, all of which were conducted at the University of Huelva (Huelva, Spain), completed this second phase of analysis.

The mineralogical composition of the black shales was semi-quantitatively determined using X-ray diffraction. Twelve samples distributed along the studied section (Fig. 3) were pulverized and analysed in the Central Research Service, University of Huelva, with a Bruker D8® Advance Diffractometer (Bruker, Billerica, MA, USA) using CuK α radiation (40 kV; 30 mA) in a 2 θ range of 5 to 70°.

Twenty-three black and dark shale samples (Fig. 3) were analysed for the identification of environmental anomalies. The samples were pulverized with an agate mill and mechanically split into aliquots of 20 g at the University of Huelva. Pulped samples were chemically characterized by analysing major and trace elements together with carbon (C) and sulphur (S) in a fully certified commercial laboratory (ALS Geochemistry Laboratories, Seville, Spain). The total abundance of major oxides was determined using inductively coupled plasma emission spectrometry (ICP-ES). Rare earth and refractory elements were analysed using ICP mass spectrometry (ICP-MS). Both procedures followed Li-metaborate/tetraborate fusion and dilute nitric digestion of samples weighing 0.2 g. Sample splits of 0.5 g were analysed after undergoing aqua regia digestion. Sulphur content, total C and TOC (total organic carbon) were determined by Leco analysis.

Analytical results were normalized to Al to avoid the dilution effect related to the disparate proportions of biogenic components and to facilitate their comparison to a standard (Calvert & Pedersen, 1993). The selected standard was the Average Shale (Mason, 1982) because it best fits the geochemical characteristics of the analysed black shales. The enrichment factor (EF) of any given element in relation to the standard was calculated using the following expression defined by Algeo & Tribovillard (2009):

$$EF_{\text{element X}} = X/Al_{\text{sample}}/X/Al_{\text{average shale}}$$

The chemical index of alteration (CIA) was calculated according to the method proposed by Nesbitt and Young (1984), taking into consideration that the calcium (Ca) included in silicates was quantified using the method by Nesbitt (2003):

$$CIA = 100(Al_2O_3/(Al_2O_3+Na_2O+CaO+K_2O))$$

For palynofacies analysis, 21 of the 23 shale samples analysed geochemically (Fig. 3) were processed following the conventional HF/HCl extraction procedure described by Wood *et al.* (1996). After undergoing acid digestion, the organic residue was mildly oxidized

with fuming nitric acid (1 min) to eliminate pyrite and remove the smallest organic particles. Then, the residue was dried and mounted in slides using Cellosize (Dow Chemical Company, Midland, MI, USA) as the dispersing agent and Elvacite (Dow Chemical Company) as the mounting medium. The analysis was performed by counting 500 organic particles per slide and the different palynological groups were quantified in percentages.

The statistical analysis of all the organic component groups was performed through the hierarchical clustering of the frequencies of organic particles, using the agglomerative Ward's method and Euclidean distances as measurements. The result was a dendrogram of four final groups with a high cophenetic coefficient (Fig. 4) that agree with the interpreted sedimentary environments.

Light microscopy was performed at the Department of Earth Sciences, University of Huelva, using a Nikon Labaphot-2 microscope with an attached Nikon DS-Fi1 digital camera (Nikon, Tokyo, Japan; software NIS Elements, F Package, 3.22.00). The classification of organic components followed the schemes of Tyson (1995) and Batten (1996).

Petrographic analysis in reflected white light of the organic matter from 15 samples (Fig. 3) was conducted at the Instituto Nacional del Carbón (INCAR-CSIC, Spain), following a modification of the standard sample preparation procedures described in ISO 7404-2. Samples crushed to a size of 1 mm were embedded in synthetic resin and mounted in cylindrical moulds. These were cut perpendicular to the base and polished. The resulting blocks were studied after 2 h in a dryer. The analysis of the organic matter in reflected white light was carried out using a X50 oil immersion objective ($n = 1.518$) of a Leitz MPV compact microscope under monochromatic light (548 nm). Microphotographs were taken with a Leica DFC420 C camera coupled to a DM 4500P Leica (Leica Camera, Wetzlar, Germany). This microscope was also used for observations in fluorescence mode.

THE FF LES VILELLES SECTION

The FF Les Vilelles section hosts the geochemical, environmental and palynological anomalies analysed. The section is named after the Les Vilelles unit and its chronostratigraphic position, immediately below the Frasnian–Famennian boundary (Fig. 2). This naming procedure is common in other analogous studies (i.e. Walliser, 1996; Racki, 2012; Becker et al., 2016). The FF Les Vilelles section consists of a succession of shales, sandstones and, to a minor extent, siltstones that vary in proportion throughout the sequence (Fig. 3).

The sandstones, which are fine-grained and well-sorted, feature a framework of quartz grains with subordinate titanite, tourmaline, Fe-oxides and zircon grains (Colodrón *et al.*, 1979). Although contacts between grains are sutured, there are no signs of coating or overgrowth, and their rounded original shapes can still be distinguished. These rocks are quartz arenites, according to the classification scheme of Pettijohn *et al.* (1972). They are rich in primary and soft-sediment deformation structures and exhibit variations in thickness, external geometry and strata stacking patterns. Macrofossils and ichnofossils are absent, although bioclasts (mostly conodont elements) and wrinkle structures are locally abundant (Fig. 3). Siltstone beds generally occur near the top of the section, forming decametric strata with signals of diagenetic silicification. Their primary syn-sedimentary characteristics are still distinguishable.

The shales are dark to black in colour, with fissile behaviour and penetrative foliation. According to x-ray diffraction (XRD) analysis, their mineralogical composition is dominated by quartz, albite, chlorite, illite and muscovite (Table 1). The absence of chlorite in samples KW-24 and KW-25 is particularly noteworthy. Their organic matter content is highly variable but generally scarce, with TOC content ranging between 0.12 and 13.3% (more details in the *Geochemistry* section). Petrographically, the organic fraction is fairly homogeneous, with

vitrinite-like and inertinite-like macerals as major components and liptinite (algal fragments) presents in minor proportion and randomly recovered. In addition to the macerals, most samples include small amounts of bitumen; derived from the thermal degradation of the original organic matter, and more rarely, oil exudates and pyrobitumen, which originated during the thermal cracking of oil. Only the lowermost analysed sample of the section (KV-2) shows exudates with intense orange fluorescence, which are probably associated with the thermal evolution of primary marine organic matter (Batten, 1996). In general, the organic matter occurs interstratified with the inorganic fraction.

The palynological record of the FF Les Vilelles section reveals the common occurrence of terrestrial and marine-derived palynomorphs (Table 2; Fig. 5). The most abundant organic components reported are equidimensional phytoclasts and spores, although some intervals are also dominated by amorphous organic matter (AOM). The rest of the terrestrial (lath-shaped phytoclasts and fungal hyphae) and marine structured organic particles (acritarchs and prasinophyceae) are subsidiary in most cases. The preservation of organic particles varies from sample to sample, which makes it difficult to distinguish between particles degraded primarily in relation to oxic, high-energy environments and those degraded during diagenetic or post-depositional weathering processes.

FACIES ASSOCIATIONS

After integrating sedimentological and palynological data, five facies associations were identified in the FF Les Vilelles section. Given that each facies association corresponds to a specific interval of the section, they reflect the record of different depositional sub-environments. The main characteristics of each facies associations is summarized and illustrated in Table 3 and Fig. 3. Their field aspect is shown in Figs 6, 7 and 8.

Facies Association 1 (FA-1): Inner shelf

Description

Facies Association 1 is found in an interval, greater than 4 m thick, at the base of the FF Les Vilelles section (Table 3; Fig. 3). It is shale-dominated and includes subordinate sandstone beds and minor siltstones that are rhythmically intercalated (Fig. 6A to C). The shale layers are 2 to 8 cm thick, structureless, and pale brown in colour due to weathering. When unweathered, they consist of dark and black shales with pyrite occurring as scattered, very fine cubic crystals; as framboids, isolated or grouped in very distinctive clusters; or as pyritized microphytoplankton, radiolarian and other unidentified microfossils (Fig. 6D and E).

Most sandstone beds are 0.5 to 3.0 cm thick and display tabular geometries with sharp bases and gradational tops. Internally, they appear as two parts sharply separated by an internal erosional surface: (i) a horizontally laminated lower part, that occupies 70 to 75% of the total thickness; and (ii) an upper part where the sandstones grade into shales. In minor amounts, 2 to 5 cm thick sandstone beds with wavy and sharp tops are also present (Fig. 6B to C). They have slightly asymmetrical external contours and internal ordering consisting of hummocky cross-stratification (HCS) comparable to the anisotropic hummocky cross-stratification layers described by Dumas & Arnott (2006). Bases from both sandstone beds occasionally include small scour marks and mud injections structures. Bioturbation was not observed.

Apart from the rhythmic alternation of shales and sandstones, the bulk of FA-1 does not appear to describe any sequential pattern. Only at the uppermost part of the interval the sand/shale (s/s) ratio increases progressively to form wavy stratification (in the sense of Reineck & Singh, 1975) that represents the progressive transition to the following facies association.

The palynofacies (Figs 5 and 9) are dominated by amorphous organic matter (AOM) (43 to 62%) characterized by exudates with intense orange fluorescence (i.e. sample KV-2). They also include subordinated amounts of equidimensional phytoclasts, acritarchs, prasinophyte phycmata and miospores. The content of marine palynomorphs (acritarchs and prasinophyte phycmata) is the largest in the section, with values up to 21%. The absence of lath-shaped phytoclasts and fungal hyphae is likewise noteworthy. The dendrogram resulted from the hierarchical clustering of the organic particles frequencies clusters all the samples from FA-1 in a compact group (Fig. 4).

Interpretation

This facies association was deposited on a platform dominated by mud sedimentation periodically interrupted by the deposition of centimetre thick sand layers. The horizontal lamination and micro-HCS of the sandstone beds are products of traction-deposition processes from bottom storm currents (i.e. Dott & Bourgeois, 1982; Tinterri, 2011) trapped in the muddy platform as thin storm beds. Similar depositional mechanisms have been proposed by Dumas & Arnott (2006). The deposition of mud was probably a combination of gravitational settling and accretion of mudstone beds from migrating floccule ripples associated to storm-induced flows, in the sense of Macquaker & Bohacs (2007), Schieber *et al.* (2007) and Schieber & Southard (2009). Both interpretations can be applied to FA-1; the first one applies to the sandstone layers with diffuse tops that exhibit parallel lamination and graded bedding, and the second applies to the micro-HCS sandstone beds with wave and sharp tops. The absence of signs of current reworking, such as wave ripples, suggests deposition below the fair-weather wave base (Vaucher *et al.*, 2017, and references therein). The increase in the s/s ratio toward the top of FA-1 represents the gradual change from the inner shelf to the nearshore; that is, from offshore to offshore-transition zone according to Reading (1996) and Clifton (2006), among others.

The mixed occurrence of terrestrial and marine palynomorphs detected in the palynological analysis also supports a marine depositional environment where storm currents supplied miospores and mostly equidimensional phytoclasts (Tyson, 1995). These environmental conditions justify the absence of lath-shaped phytoclasts and fungal hyphae in the shales from FA-1, because such organic particles require a low energy and terrestrially influenced environment to be deposited in (Hart, 1994). The nature of the AOM is difficult to evaluate by light microscopy but the co-occurrence of non-fluorescent AOM particles and particles showing intense orange fluorescence suggests a mixed continental/marine origin (Bertrand *et al.*, 1986, Batten, 1996). The high AOM proportion in the shales from FA-1 envisages a muddy platform with elevated organic productivity and high potential for preservation. Such characteristics, together with the abundance of framboidal pyrite and the occurrence of pyritized microfossils, are indicative of hypoxic environmental conditions and intense bacterial activity below the sediment-water interface (Bernier, 1970; Davis *et al.*, 1988, 1989; Tyson, 1995; Wignall *et al.*, 2016).

Facies Association 2 (FA-2): Shoreface

Description

Facies Association 2 (Table 3; Fig. 3) is linked to an interval *ca* 2 m thick that gradually overlies FA-1 deposits. The entire interval consists of a thickening upward sequence with shale-dominated heterolithic facies at the base and sand-dominated deposits from the middle part to the top. It is made up of three successive facies sharply separated by laterally continuous shale layers, 8 to 10 cm thick (Fig. 7A and B), that include streaks and very flattened lenses of fine sandstone similar to the 'laminated sand-streaked mud' of De Raaf *et al.* (1977)

Facies from the lower part of the interval include wavy bedding in the sense of Reineck & Singh (1975), with centimetre thick sandstones and shales showing s/s ratios equal to, or slightly above 1. The sandstone beds have sharp bounded surfaces with plane bases and undulating tops. Internally, they show symmetrical and asymmetrical cross-bedding and small swollen lens-like sets. Internal erosive surfaces discriminate truncated ripples. The following facies consist of flaser bedding made of decimetre thick sandstone beds, internally showing aggradation of small current and wave bedforms, and shale drapes, 1 to 2 cm thick, that bifurcate to seal internal lamination and stratification surfaces. Undulate lamination and HCS complete the internal ordering of these sandstone beds. The facies from the upper part of FA-2 consist of amalgamated sandstone beds that form packages up to 40 cm thick and exhibit undulating external geometry. Internally, they contain well-developed HCS and swaley cross-stratification (SCS), *ca* 30 cm in wavelength, and gently asymmetrical undulating laminations. These can include small oscillation ripples at the top, 3 to 4 cm in wavelength. Internal erosional surfaces and signal of soft-sediment fluid escape are frequent.

Palynofacies of samples from FA-2 (Figs 5 and 9) show a drastic reduction in AOM (<5%) and an increase in the proportion of equidimensional phytoclasts (65 to 84%), if compared with samples from FA-1. The miospore group also experiences a slight increase (13 to 24%) and the microphytoplankton content progressively decreases until values are below 10%, although they never disappear. Small amounts of lath-shaped phytoclasts (values below 4%) are recorded for the first time. Finally, it is significant that the fungal hyphae are still absent. The cluster analysis of the organic particles groups the samples from this interval with those from the subsequent facies associations FA-3 and FA-4 (Fig. 4).

Interpretation

The three facies described in FA-2, wavy, flaser and undulate-tabular bedding, depict a shallowing-upward sequence that denotes a progressive increasing in the depositional energy and sand supply (Clifton, 1981, 2006). The dominant sedimentary structures in the sandstone beds are symmetrical and asymmetrical ripples, HCS, SCS and undulate lamination; they suggest deposition under oscillatory flow conditions (Heward, 1981). The centimetre scale sandstones-shales alternation from the lower part is similar to that from the top of FA-1. It indicates deposition above storm wave base and below, or very proximal to, fair-weather wave base. The amalgamated sandstone beds with undulate lamination, HCS, SCS and abundant wave ripples from the upper part suggest the generation of sand bars above fair-weather wave base (Clifton, 2006; Tamura, 2012). The absence of sedimentary structures such as planar or low angle cross-lamination locates this interval below the swash zone (Greenwood & Mittler, 1985). Consequently, the depositional environment represented in FA-2 evolved from a muddy/sandy and flat offshore-transition to a fine-sandy barred shoreface. The laterally continuous shale layers, 8 to 10 cm thick, that sharply separate the sandstone intervals (Fig. 7B) are interpreted as interbar trough deposits, probably associated with progradational episodes (Otvos & Carter, 2013; Martini 2014

A deposit related to tidal currents in a wave-influenced and tide-influenced littoral environment, similar to those studied by Basilici *et al.* (2011), Vakarelov *et al.* (2012) or Vaucher *et al.* (2017) cannot be categorically excluded. However, the first interpretation seems to be more appropriate for FA-2 because clear evidence of tidal influence, similar to that described by Visser (1980); Davis & Darlymple (2012) or Longhitano *et al.* (2012) were not found, other than shale drapes and flaser stratification. The use of flaser structures as indicators of tidal environments can furthermore lead to erroneous interpretations, as Martin (2000) documented in his study of flaser fluvial sediments. Regarding the palynological record of FA-2, the significant contribution of phytoclasts, small amount of microphytoplankton and the virtual absence of AOM are also characteristic of high-energy,

well-oxygenated coastal environments, typically wave-dominated (Tyson, 1995; Mendonça Filho *et al.*, 2011).

Facies Association 3 (FA-3): Beach face versus beach foreshore

Description

Facies Association 3 (Table 3; Fig. 3) is defined in a 1.4 m thick interval, in sharp contact with the underlying FA-2 (Fig. 7A). It is sandstone/shale-dominated at the base and sandstone-dominated from the middle part to the top. It shows a conspicuous thickening upward sequence composed by three facies: (i) centimetre scale shale levels that are occasionally streaked and rarely include minor isolated and flattened climbing-ripples; (ii) centimetre scale bidirectional rippled sandstone beds with micro-hummocky, undulate and symmetrical cross-stratifications; and (iii) sandstone packages of amalgamated tabular sandstone beds, 12 to 15 cm thick each, with slightly scoured bases and occasionally undulated tops. Internally, these beds consist of the superposition of flat and horizontal sets with parallel lamination (planar stratification, *sensu* Harms, 1975) and undulate lamination in minor extend. Internal erosional surfaces are frequent. Foreset lamination of small symmetrical ripples can also occur. Shale drapes are absent. The palynofacies of the single shale sample analysed within this facies association (KV-11) is virtually equivalent to those from FA-2 (Figs 4 and 9).

Interpretation

The thickening and shallowing-upward sequence described in FA-3 indicates the increasing influence of waves and storms on the coastal seafloor and a rapid increase in the s/s ratio of the middle and upper parts of the interval (Clifton, 1981, 2006). The most characteristic facies of FA-3 are sandstone tabular packages from the upper part. They consist of the amalgamation of decimetre thick flat beds with planar lamination, occasionally topped by undulate lamination, that are frequently interrupted by internal erosive surfaces. Both types of laminations are large-scale structures generated by strong currents at very shallow depths

(Clifton, 2006, and references therein). Both are respectively associated to the upper plane beds and the sand waves occurring in the surf and swash zones (Southard 1975, Greenwood & Mittler, 1985; Dumas & Arnott, 2006). These deposits are therefore interpreted as flat sandbars equivalent to the shoreline sands observed by Weimer *et al.* (1982). The tabular geometry of the packages suggests the high capacity of wave and storm currents for levelling and flattening the surface beach, thus generating 'swash surfaces'. In consequence, the depositional setting interpreted for FA-3 is a beach face environment (beach foreshore after Walker & Plint, 1992 and nomenclature from Clifton 2006). In this context, the very shallow waters behind the breaking point reduces the wave orbital diameter of storm and wave currents (Yang *et al.*, 2006). This could explain the small size of symmetrical ripples, HCS and other sedimentary structures in the intermediate facies of FA-3.

The centimetre scale shale levels, occasionally streaked, that include minor isolated and flattened climbing-ripples from the lower part of FA-3, were deposited under low energy conditions immediately after storm, flood or even fair-weather periods (Rine & Ginsburg, 1985; Yang *et al.*, 2005; Vakarelov *et al.* 2012). The low preservation potential of these kind of deposits (Li *et al.*, 2000) requires areas protected, or relatively protected from currents, such as interbar troughs, in order to be preserved. This scenario is compatible with the shoreface-attached sand ridges in a progradational wave-dominated open littoral or barrier island models by Clifton (2006) and references therein).

The shallowing-upward sequence that represents FA-3 records rapid coastal progradation from the shoreface to the beach face. This littoral environment was characterized by the occurrence of smooth sandbars at the beach area and a foreshore with no clear evidences of tidal influence. This is a beach foreshore according to Walker & Plint (1992) and Clifton (2006).

Facies Association 4 (FA-4): Overwash zone

Description

Facies Association 4 (Table 3; Fig. 3) is composed of shales, sandstones and sand-rich shales, more than 3.5 m thick. It overlies FA-3 by means of a sharp and flat contact and exhibits an apparently chaotic aspect produced by the disappearance of the geometrical and sequential ordering characterizing the subjacent intervals (Fig. 7C and D). The internal ordering of this facies association is nevertheless recognized when meticulously examined.

Sandstones mostly occur as sand-rich packages up to 50 cm thick composed of decimetre thick sandstone beds with undulated morphology related to HCS and SCS (Fig. 7C). Thinner and isolated sandstone beds are also present although in minor proportions (Fig. 7D). They commonly pinch out, have distinct undulating geometry, and frequently include mica-rich top laminae with wrinkle structures similar to those described by Hagadorn & Bottjer (1997) and Noffke (2009). Soft deformed sand/shale-rich levels also occur.

The shales display: (i) sparse decimetre thick levels that are laterally continuous but with local constrictions; (ii) laterally discontinuous levels encapsulated between sandstone beds within the sandstone packages; (iii) thin drapes within sandstone beds; and (iv) centimetre thick lenses over sandstone bed antinodes.

The palynological content of the two shale samples analysed within FA-4 is characterized by a large proportion of continental palynomorphs (Fig. 9). The spore contents are 2% and 10% and equidimensional phytoclasts are 85% and 67%. The lath shaped phytoclasts is below 4%, and the fungal hyphae, that occur in FA-4 for the first time, is around 1%. The marine phytoplankton and AOM frequency is also very low. The hierarchical clustering of the organic particles shows that the shale samples from FA-4 are grouped together with samples from FA-2 and FA-3 (Fig. 4).

Interpretation

The palynological record of the shales from FA-4, with a very high proportion of equidimensional phytoclasts and very rare microphytoplankton strongly suggest a sedimentary environment with high continental and low marine influence (Batten, 1996). The mud was partially deposited under very low energy conditions.

On the other hand, the HCS and SCS of the sandstone beds are indicative of a depositional environment dominated by oscillatory and unidirectional flow conditions (e.g. Dott & Bourgeois, 1982; Swift *et al.*, 1983; Duke, 1985; Cheel & Leckie, 1993; Quin, 2011). The thin and discontinuous shale drapes within the internal layers of the HCS and the centimetre thick shale beds accumulated at the scooping surfaces of the swaley morphologies suggest the absence of later reworking. Accordingly, FA-4 consists of a pile of storm layers trapped within muddy sediments that were unaffected by wave currents. Similar depositional mechanism has been described by Atwater (1987), Switzer *et al.* (2005), Lange & Moon (2007) or Wang & Horwitz (2007) for storm and tsunami deposits on the coastal plain. Although uncommon, deposition of hummocky beds in water depths shallower than fair-weather wave base level, in the coastal plain, or even within lacustrine littoral environments has been reported (i.e. Greenwood & Sherman, 1986; Basilici *et al.*, 2011; Soria *et al.*, 2014). In consequence, FA-4 can be confidently interpreted to reflect high-energy apron deposits in the overwash zone, inland from the shoreline sands.

Facies Association 5 (FA-5): Lagoon

Description

Facies Association 5 (Table 3; Fig. 3) is an interval, ca 7 m thick, located in the uppermost part of the FF Les Vilelles section, in gradual contact with the subjacent FA-4. It is composed of dark/black shales with parallel laminated sandy streaks and decimetre thick silicified siltstone beds (Fig. 8A). The siltstone beds exhibit very thin horizontal lamination caused by small grain-size differences.

One 30 cm thick, distinct and isolated-sandstone bed, with a wavy surface and up to 130 cm in wavelength, is embedded within the lower part of FA-5. Internally, it exhibits planar lamination, HCS and a thin interval with undulating lamination that is in phase with the external bedform morphology (Fig. 8B). Under the microscope, it exhibits a pelletoidal texture consisting of uniform, millimeter scale lumps of fine sandstone embedded in masses of organic matter (Fig. 8C). Coarse carbonaceous particles and bioclasts of conodont elements, tentaculitids and algal oncoids are also present (Fig. 8D). The siltstone beds surrounding this wavy sandstone bed also include sand-sized bioclasts of conodont elements that are oriented parallel to lamination and wrinkle structures that are related to bacterial mats, similar to those described by Noffke *et al.* (2003) and Parizot *et al.* (2005).

The palynological record of the shale samples from FA-5 shows an upward increase in the proportion of spores (22 to 54%) although the equidimensional phytoclasts still dominate the assemblages (39 to 67%). The lath-shaped phytoclasts and well preserved fungal hyphae (Fig. 8E) reach their maximum proportions, at 20% and 9%, respectively. Marine organisms, with values below 2%, remain very poorly represented (Fig. 9).

Sandwiched at the upper part of FA-5 is a 130 cm thick level that depicts a clearly different palynofacies. Here, shale samples (KV-23, KV-24 and KV-25) show a drastic increase in the proportion of AOM (up to 85%) and a reduction in the numbers of miospores and equidimensional phytoclasts (Fig. 9). Interestingly, the lath-shaped phytoclasts and fungal hyphae roughly preserve the same frequency. The AOM exhibits a very weak fluorescence and no marine particles were recorded during counting. Nevertheless, the petrographic analysis of the samples from this AOM-rich level detected the occurrence of some marine algae. The cluster analysis of the organic particles also reveals two distinct groups in FA-5, one for the AOM-rich samples and the other for the rest of samples from the

interval (Fig. 4). As explained in the geochemistry section, this AOM-rich level also features intense geochemical anomalies.

Interpretation

Lithofacies from FA-5 consist of a predominantly shaly interval with minor sandstone and siltstone intercalations that form millimetre to centimetre scale beds with subtle parallel lamination. The palynological content is characterized by the common occurrence of very thin fungal hyphae and lath-shaped phytoclasts. Both sedimentological and palaeontological evidence clearly points to a quiet environment close to parent plants. Since the occurrence of marine algae precludes a purely terrestrial environment, a restricted low-energy lagoonal setting with swamped deposits, such as that defined by Davies *et al.* (1971), McGowen & Scott (1975), Swift (1975) or McCubbin (1982), is proposed as the most plausible scenario. Moreover, the very low proportion of marine-derived palynomorphs and the significant contribution of the miospore content are also indicative of restricted, low-energy lagoonal environments (Pieńkowski & Waksmundzka, 2009; Souza *et al.*, 2016).

At the lagoonal rim, storm episodes rich in marine particles arrived as weak bottom currents. These currents generated silt layers that were remobilized afterward by subtle wind waves. During remobilization, the matrix of the silt layers was removed and the conodont elements were resuspended and redeposited at the top of the layers. This process was demonstrated through experiments by Broadhead *et al.* (1990).

The wavy sandstone bed at the base of FA-5 is interpreted to reflect one single highly energetic event, either a storm or a tsunami surge, that was trapped at the rim lagoonal muds. The depositional mechanism, as modelled by Bourgeois *et al.* (1988) and Einsele *et al.* (1996), and more recently by Scasso *et al.* (2005), Dawson & Stewart (2007) and Morales *et al.* (2008), involves the inland displacement of high-energy currents that are rich in marine sediments. These produce the mixing of terrestrial and marine components and the

resuspension of organic matter and fine particles in the lagoonal pond. It is difficult to categorically discriminate between a storm-related or a tsunami-related origin, but, based on the inland location of the deposit, the sediment source and the distribution patterns, which follow the model proposed by Morton *et al.* (2007). In the current study, this deposit is interpreted to represent a tsunamite rather than a storm layer. In that sense, the syn-orogenic character of these Devonian deposits, framed within the Variscan orogeny context (Franke, 2000; Wicander & Monroe 2016; Nance *et al.*, 2010), support this interpretation.

In the inner lagoon, the marine influence declined, favouring the development of a swamped environment almost exclusively dominated by terrestrial input. Here, a sudden and sharp anoxic episode, represented by an AOM-rich level, occurred. Above this level, the AOM content decrease to values below 10% (samples KV-26 and KV-27), suggesting that the system turned oxic again.

GEOCHEMISTRY

Analytical data of the shale samples from the FF Les Vilelles section are included in Table 4, and their respective location in the stratigraphic log is illustrated in Fig. 3. The Pearson's correlation coefficients between representative elements are shown in Table 5. Analysis and interpretation of these data provide information concerning the sedimentary environment and other processes synchronous with deposition.

Source area and clastic input

The influence of the source area on the chemical composition of shales is determined not only by the nature of the rocks but also by environmental conditions, particularly the climatic conditions that govern weathering and the subsequent transport of sediments to depositional environments (Sageman & Lyons, 2003).

The Ti–Th–Hf ternary diagram (Fig. 10), which was designed for the analysis of conservative elements in sedimentary processes (modified from McLennan *et al.*, 2003), shows that the Les Vilelles samples plot as a narrow cluster, suggesting a single source area with a uniform lithology. This cluster falls within the ranges of the Average Shale of Mason (1982) and the Continental Crust (Wedepohl, 1995), with values surrounding the compositions of the Greywacke standard (Wedepohl, 1995) and the Post-Archean Australian Shale (PAAS) of Taylor & McLennan (1985).

Concerning the weathering processes at the source area, the Nesbitt & Young (1984) chemical index of alteration (CIA) depicts high values (68 to 80%). Only samples KV-23 to KV-25, which were obtained from the AOM-rich level at the lagoonal pond (in the upper part of FA-5), yield values ranging between 56% and 62%. When plotted on the A–CN–K and A–CNK–FM diagrams (Fig. 11), most of the samples cluster homogeneously near the compositions of PAAS, except for samples from the inner shelf (FA-1), which are slightly deviated to apex A. Samples with low CIA values from the AOM-rich level are not included within this cluster. They instead group around the AS standard on the A–CN–K diagram (Fig. 11A) and close to the granite-rhyolite standard composition on the A–CNK–FM diagram (Fig. 11B). Given that these samples are located near the top of the section, it is possible to envision a radical change in the weathering conditions occurring at the source area during a short, sporadic episode. The high $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio of these samples (Fig. 12) suggests an increase in the physical weathering processes, which could be related to climate change, volcanic activity, wildfires or tectonic uplift (Nesbitt *et al.*, 1980). The small amount of inertinite macerals argues against forest wildfires as the dominant process. The geochemical homogeneity of the source area contradicts the possibility of significant volcanic activity, and the quick recovery of former weathering conditions rejects the tectonic uplift hypothesis. Consequently, an episode of aridity is the most plausible factor explaining this weathering disturbance.

The correlation of the most significant elements composing the analysed black shales with respect to Al (Table 5), which is an element considered to be representative of detrital input (Riquier *et al.*, 2006), yields high values ($r > 0.8$) for K, Ti, Ba, Th and Sc; low values for other elements commonly related to fluvial input, such as Zr, Mg and Fe; and negative values for Si. Silica also exhibits very low to negative correlation with other major elements. This, together with the mineralogical data discussed above (Table 1), suggest that the main terrestrial input is essentially comprised of dioctahedral phyllosilicates of the illite/muscovite type. The negative correlation of Si with other elements suggests that silicification could be associated with either organic activity or diagenesis.

The vertical variation of the elements most significant for the analysis of clastic input is illustrated in Fig. 12. The Ti/Al ratio remains constant throughout the section, with only minor negative inflexions at the log base. In sedimentary processes, Ti behaves conservatively (Zao & Zheng, 2015) and can reach the basin in the granular fraction either as oxide minerals (ilmenite, rutile or spinel group minerals) or as inclusions within phyllosilicates such as leucoxene. At Les Vilelles, the excellent correlation of Ti with Al and K suggests that the latter option is the most plausible. The small negative anomalies at the base of the section are explained by the dominance of chemical weathering at the source area of the inner shelf. This is also shown in the A–CN–K diagram (Fig. 11A). The determining factor most strongly controlling the behaviour of Zr in sedimentary processes is transport, because the main carrier of Zr (zircon) is a dense mineral that is chemically very stable and highly resistant to abrasion. Given these properties, Zr is separated during transport and concentrated in the granular fraction. The relationship between Zr and Al is basically conditioned by the amount of small inclusions within phyllosilicates. In the FF Les Vilelles section, the Zr/Al ratio shows minor differences, with only a positive anomaly occurring at the top of the AOM-rich level. This higher amount of Zr could be related to the occurrence of more intense physical weathering at the source area or the aeolian transport of fine particles (Taylor *et al.*, 1983; McLennan *et al.*, 2003). Finally, the Na/K ratio shows

small variations depending on its facies associations. When compared to the stratigraphic log, it is correlated (although only slightly) with differences in the s/s ratio. Only at the top of the section do samples from the AOM-rich level depict very anomalous values that are interpreted to be related to climate change. This favours physical weathering and the preferential supply of plagioclase to phyllosilicates, as indicated by the mineralogical data in Table 1.

Bioproductivity

The evaluation of the geochemical record of bioproductivity is still an open issue, given the polyvalence of the most commonly used proxies. Some of these proxies include P, excess Si and Ba (Schmitz *et al.*, 1997; Pujol *et al.*, 2006), and the elemental ratios of Cu/Al and Ni/Al (Tribovillard *et al.*, 2004; Riquier *et al.*, 2006). Phosphorous, which is essential in metabolic reactions, also forms part of the skeleton of vertebrate animals. Nevertheless, it is difficult to use P as a proxy for bioproductivity because it can occur within heavy minerals (xenotime and monazite) and because the intrabasinal redistribution of apatite-bearing skeletal fragments of organisms (for example, conodonts) is a common process.

In the shales from the FF Les Villes section, the correlation of Al with elements generally associated with bioproductivity (i.e. Cu, Ni, Ba and Si) is erratic, with the exception of Ba, which shows high correlation coefficients (>0.90) with both Al and K (Table 5). This suggests its association with phyllosilicates of the illite–muscovite type. Trace elements associated with enzymatic and/or metabolic processes, such as Cu, Co and Ni (Wackett *et al.*, 2004) yield cross-correlations coefficients of approximately 0.7 for both Cu/Ni and Cu/Co and 0.9 for Co/Ni.

Normalized P_2O_5/Al_2O_3 values comprise a heterogeneous profile with a strong peak related to sample KV-1, which was collected from the inner shelf (Fig. 12). Its normalized REE spectrum (Fig. 13) resembles that of the apatite recovered from Devonian conodont elements (Girard & Albarede, 1996). The other proxies analysed show broadly coherent

behaviour for most of the samples. Barium is affected by the dilution effect because part of it arrived at the basin as detrital influx. Copper, Ni and to a lesser extent Si depict positive anomalies in some of the shale samples from the lagoonal pond (excluding the AOM-rich level), and another, more discrete positive anomaly is present in samples from the shoreface and beach face (Fig. 12). This suggests that small increasing pulses of bioproductivity occurred during the sedimentation of the FF Les Vilelles section, with the most distinctive pulse located at the very top, just at the end of the lagoonal interval. Copper and Ni also evidence strong positive excursions coinciding with this interval.

Redox conditions

The proxies most commonly used in the study of authigenic components are elements controlled by the redox conditions of the sedimentary environment, such as Mo, U, Mn and Re (Lyons *et al.*, 2009, and references therein). In the study area, the disparate correlation of these elements with TOC is indicative of a complex geochemical system (Table 5). Uranium shows negative correlation with elements commonly associated with detrital input, such as Al, K and Th, and positive correlation with P, C, Y, Sr and Mo, suggesting an exclusively authigenic origin. The relatively high correlation coefficients for P and REEs suggest that part of this U could be fixed in the apatite lattice. However, the positive correlation of U with TOC, other redox-sensitive elements also strongly associated with TOC, such as Mo, and some chalcophile elements, such as, Hg and Pb, suggest that its abundance is mostly controlled by the redox conditions of the environment.

The variation of the redox conditions throughout the FF Les Vilelles section (Fig. 12) was observed by using the Mn/Al ratio in addition to other proxies that show strong affinities with organic matter. The negative anomalies of Mn suggest a generalized reducing environment for the inner shelf and lagoonal pond, while its positive anomalies are indicative of moderately oxidizing conditions in the nearshore (shoreface, beach face and overwash zone). Regarding the organic-sensitive proxies, small anomalies of TOC, U and Re have

been recognized on the inner shelf. Samples from the nearshore display an evolution from slightly anoxic/sub-oxic to well oxygenated conditions that is compatible with the aforementioned behaviour of Mn. These oxidizing conditions prevailed at the lagoon until the deposition of the AOM-rich level. At this point, all of the described proxies suffered strong positive excursions.

Figure 14 illustrates the covariation of the enrichment factors of U (UEF) and Mo (MoEF) for the shales of the FF Les Villedes section. Two samples from the inner shelf yield UEF values close to one and slightly negative MoEF values. The other three samples are enriched in U, and one of them (KV-1) yields UEF values close to 10. Their Mo content is normal for shales (MoEF \approx 1). Samples from the nearshore and some samples from the lagoonal pond cluster around one for both parameters. In contrast, the three samples from the AOM-rich level exhibit strong positive anomalous values.

In summary, the sedimentary environment evolved from anoxic/sub-oxic conditions in the inner shelf to oxidizing conditions in the nearshore zone and the lagoonal rim. Then, the system suffered a severe anoxic crisis, but conditions turned oxic again at the top of the section, as indicated by the normal values of the redox proxies presented here.

Hydrothermal input

The hydrothermal input is manifested along the section by its enrichment in chalcophile elements such as Pb, As and Hg (Fig. 12). Under natural conditions, large amounts of Arsenic and mercury can reach the sedimentary environment or escape to the atmosphere during the passive degasification of volcanic–subvolcanic magmatic systems (Hedenquist *et al.*, 1993; Hedenquist & Lowenstern, 1994; Goff *et al.*, 1998), subaerial fumaroles (Engle *et al.*, 2006) or hydrothermal submarine activity (Stoffers *et al.*, 1999). In sedimentary environments, these elements have a strong affinity for organic matter, and consequently, frequently accumulate in C-rich sediments. The high abundance of these elements observed

in some samples is probably related to the coupled action of hydrothermal or fumarolic activity together with the tendency of such elements to bind with organic matter to form organometallic compounds. The vertical distribution of the normalized values of these elements (Fig. 12) indicates that three pulses of fumarolic/hydrothermal activity occurred along the section, with the last and most intense one coinciding with the strong anoxic peak in the AOM-rich level.

DISCUSSION

Sedimentary environment

The FF Les Villes section (Fig. 3) consists of a 20 m thick, shallowing-upward sequence composed of sandstones, siltstones and shales deposited mostly above the fair-weather wave base in a regressive coastal environment. Sedimentological and palynological evidences, including here the cluster analysis of the organic particles, permit the identification of five facies associations along the studied section, suggesting the evolution from an inner shelf to the lagoonal pond within the coastal plain. Sedimentary processes in the nearshore zone and even in the proximal lagoon were mostly associated with storm and wave currents, whereas the lagoonal pond was dominated by the settling of fine particles. In the inner shelf, both types of processes coexisted. Similar characteristics have been identified in other studies focusing on modern and ancient deposits formed in proximal regressive storm/waves-dominated environments (e.g. Swift *et al.*, 1991; Walker & Plint, 1992; Brenchley *et al.*, 1993; Chakraborty & Sensarma, 2008).

The thickness of the FF Les Villes section (20 m) could be an *a priori* limiting factor for a sedimentological analysis such as the present one. Nevertheless, after scrutinizing the literature for studies of sandstone–lutite regressive sequences deposited in prograding coastal environments that evolved from platform/lower shoreface to environments behind the shoreline, this argument loses strength. The thickness of most of these sequences ranges from 3 to 10 m in the world renowned prograding sequence of Mackenzie (1972), which

occurs in the Lower Cretaceous Dakota Group, Colorado, to 35 m in the also well-known Cretaceous Gallup Sandstone sequence, New Mexico (McCubbin, 1982). Moreover, the FF Les Vilelles regressive sequence is in accordance with the shallowing-upward and low-energy coastal succession modeled by Galloway & Hobday (1996).

Within the entire section studied here, it is evident that the thickness of the lagoonal interval is larger than that of the subjacent overwash, beach face and shoreface. Apart from the tsunamite bed at the lagoonal rim, all other mud and silt deposits at the lagoon are lithologically uniform. This suggests a stratigraphic architecture driven by high sedimentation rates and strong aggradation in this part of the section, which both favour the rapid accumulation and burial of organic matter. The lagoon is thus envisaged to be a sediment trap. The orogenic framework of the CCR during the latest Frasnian most likely favoured this phenomenon and justified the common occurrence of earthquakes responsible for the formation of tsunamite beds, such as the one reported here.

Chronostratigraphical setting

The age of the entire studied section has been constrained to the latest Frasnian, immediately below the Famennian boundary. Although the absence of Famennian deposits above the section could cast doubts on the precise location of the FF boundary, it is possible to reduce such uncertainties when interpreting chronostratigraphic and sedimentological data in terms of sequence stratigraphy and sea-level curve.

The maximum regressive phase in the Late Devonian occurred during the latest Frasnian, coinciding with the T-R cycle IId of the sea-level curve proposed for Euramerica by Johnson *et al.* (1985) and Sandberg *et al.* (1988). This represents a complex cycle with several minor transgressive-regressive subcycles and a drastic sea-level fall at the top. Within this context, all kinds of deepening, shallowing, and aggrading sequences are expected. From a sequence stratigraphy perspective, the FF Les Vilelles section corresponds to a highstand system tract (Van Wagoner *et al.*, 1988; Catuneanu, 2006)

located immediately below the sequence boundary surface, which is here represented by the erosional contact with the overlying Mississippian radiolarite chert series. This sequence boundary, which involves a dramatic sea-level fall, is located exactly at the FF boundary in the studied section. Moreover, the strong environmental anomalies associated to the Kellwasser event in the studied sequence reinforce this chronostratigraphical assignation (Denayer & Mottequin, 2015; Becker *et al.*, 2016).

The Kellwasser event at the Catalan Coastal Ranges

Geochemical and palynological data reveal three different steps of anomalies at the FF Les Vilelles section, denoting increasing amounts of environmental stress. Considering the age of the section, these pulses have been assigned to the Kellwasser event (KE) and more precisely, to the Upper Kellwasser event, according to Walliser (1996). The first step of the KE in the region has been detected in the shale from the inner shelf at the base of the section. There, the geochemical proxies reflect a moderate environmental disturbance characterized by a subtle increase in bioproductivity, hydrothermal activity and dysoxic/anoxic environmental conditions (Fig. 12).

The second KE step consists of a peak in hydrothermal activity reported in the nearshore deposits (Fig. 12). The analysis of geochemical proxies indicates that the intensity of this peak was moderate. However, considering that the dominant sedimentary processes in the nearshore favoured the dissipation of geochemical proxies through seawater and atmosphere, this hydrothermal activity should be higher.

Finally, the third and most intense KE step was recorded in the so-called 'AOM-rich level' within the lagoonal interval. The geochemical proxies in this level reveal a sudden shift in the weathering regime at the source area from chemically to physically dominated, reflecting a drastic change in the climate to more arid conditions (Fig. 12). Palynofacies analysis suggests that this aridity peak triggered the partial or total denudation of the

vegetation cover, increased the erosion rates and finally favoured the deposition of large amounts of biomass into the lagoonal pond (Fig. 9). Similar erosive processes have been described by Averbuch *et al.* (2005, and references therein), although not in relation to climate disturbances but rather linked to tectonically influenced palaeogeographic changes.

In addition to aridity, the geochemical proxies in this third KE step also reveal the occurrence of hydrothermal activity and strongly anoxic environmental conditions. At the top of the section, above this last step, the environmental conditions turned oxic, and no more geochemical or palynological anomalies were recorded (Figs 9 and 12). The swamped muds were highly efficient at catching environmental anomalies, and the high sedimentation rates favoured their preservation.

Based on the data discussed above, the present study documents the Kellwasser environmental crisis in a sedimentary depositional system behind the shoreline, in the form of a stepwise and multi-causal event. The causes exposed here for the origin of the Kellwasser event have been largely alluded to in the literature, although separately. See for example, the comprehensive reviews by Walliser (1996) and Racki (2005), as well as the studies by Wignall (2001), Racki *et al.* (2002), Condie (2004), Pujol *et al.* (2006) and Chen *et al.* (2013) of hydrothermal activity and anoxia, those by Joachimski & Buggisch, (1993), Hallam & Wignall (1997) and Over *et al.* (2005) of climatic causes, and those by Chen *et al.* (2002) and Carmichael *et al.* (2014, 2016) of the increases in terrestrial sediment and nutrient input. In this last case, the required proximity of land masses was only supported by geochemical data, and the Kellwasser horizon was recorded in a shallow marine setting.

Finally, it remains unknown whether anoxia spread out from ocean bottom waters to coastal environments (see for example the hypotheses of Goodfellow *et al.*, 1989; Arthur & Sageman, 1994; McGhee, 1996), or whether the opposite process occurred (Bond *et al.*, 2004; Carmichael *et al.*, 2014). This question could be solved through the correlation of

intrabasinal and synchronous latest Frasnian sequences covering coastal, shallow and deep marine environments. In that sense, the data in this study suggest that anoxia originated in shallow marine environments, but there are no signs indicating how far this spread throughout the deep ocean. The connection between shallow and deep anoxia is an interesting issue that is raised here.

CONCLUSIONS

Based on all of the data, interpretations and discussions exposed in this study, the following conclusions can be drawn:

- The FF Les Vilelles section, located in the southern part of the Catalan Coastal Ranges (CCR), is a shallowing-upward detrital sequence dated to the latest Frasnian, immediately below the FF boundary. The sedimentological, stratigraphic and palynological analyses conducted in this section point to a prograding to aggrading sequence, with increasing accumulation rates at the top, representing the evolution from shallow marine to coastal plain environments.
- The geochemical and palynofacies analyses of the FF Les Vilelles section detected three anomalous steps, denoting increasing environmental stress, that are associated with the Kellwasser Event. These steps are characterized by fluctuations in redox conditions, clastic and hydrothermal input and bioproductivity.
- The first two steps were recorded in the inner shelf and nearshore mud deposits, respectively. The third and most intense step was detected in a 130 cm thick level of shales from the lagoonal pond. Here, the swamped muds were an efficient trap for hydrothermal fluids and organic matter, both of which favour high levels of anoxia. The geochemical proxies for clastic input also suggest that a peak of climatic aridity occurred here. This promoted the denudation of the vegetation cover, accelerated

erosional processes and finally favoured the deposition of large amounts of organic matter in the lagoon. After this episode, the environmental conditions at the lagoon turned oxic.

- Considering all of the above data, the Kellwasser was recorded in the CCR as a stepwise and multi-causal event, with the last and most intense step occurring within the lagoonal pond. This is the first time that the Kellwasser event has been reported in a sedimentary environment behind the shoreline. It is also the first time that it has been described in the CCR.

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FIGURE CAPTIONS

Fig. 1. (A) Geological sketch of the Catalan Coastal Ranges (CCR), showing the location of the central Priorat Massif. Northern (dark brown) and southern (pale brown) Palaeozoic outcrops are those referred to in Fig. 2. (B) Geological map of the study area. Modified from González et al. (2015). 1 = black shale and quartz arenite (Givetian?–Frasnian); 2 = chert (Tournaisian to early Viséan); 3 = greywacke, conglomerate, shale, limestone lenses, chert olistostromes (Viséan); 4 = shale, conglomerate, limestone lenses (Serpukhovian); 5 = shale, greywacke, conglomerate (Bashkirian-early Moscovian); 6 = conglomerate, red sandstone, lutite (Buntsandstein facies); 7 = limestone, dolostone (lower Muschelkalk facies); 8 = conglomerate, sandstones clay (Palaeogene).

Fig. 2. Lithostratigraphic chart of the Palaeozoic in the Catalan Coastal Ranges (CCR), indicating the location of the FF Les Vilelles section. 1 = metamorphized shale, sandstone and minor limestone; 2 = conglomerate; 3 = volcanic and volcanoclastic rocks; 4 = sandstone and shale; 5 = dark to black shales; 6 = limestone; 7 = chert; 8 = sandstone; 9 = black shale and quartz arenite; 10 = chert, greywacke, conglomerate, shale and limestone lenses; 11 = shale, conglomerate and limestone lenses; 12 = shale, greywacke, conglomerate. Grey diagonal lines represent stratigraphic gaps. K = Kellwasser event. For references, see *Regional Geological Setting* section.

Fig. 3. Stratigraphic log of the FF Les Vilelles section, showing the location of collected samples. To the left are facies associations (FA-1 to FA-5), sedimentary environments and age. TL = tsunamite layer; ARL = amorphous organic material (AOM) rich level; M = Mississippian.

Fig. 4. Dendrogram cluster analysis of the organic components recovered at the FF Les Vilelles section, based on the agglomerative Ward's method. The cophenetic correlation coefficient (r_{coph}) is indicated in the bottom left. ARL = AOM rich level.

Fig. 5. Microphotographs of the main organic components considered in this study. (A) Spore, *Grandispora gracilis* Higgs, 1975. (B) Spore, *Geminospira lemurata* Balme emend. Playford, 1983. (C) Prasinophyte phycocyst, *Dictyotidium fairfieldense* Playford, 1978. (D) Acritarch, *Craterisphaeridium sprucegrovense* (Staplin) Turner, 1986. (E) Equidimensional phytoclast. (F) to (H) Lath-shaped phytoclast. (J) Amorphous organic matter (AOM). (H) Fungal hypha. Scale bars represent 25 μm in (A) to (D) and 50 μm in (E) to (J).

Fig. 6. Field and microscope photographs of FA-1. (A) Outcrop view. (B) Alternation of shales and tabular sandstone beds. Coin for scale in the central area. (C) Alternation of shales and wavy sandstone beds. Coin for scale in the central area. (D) Photomicrograph of a shale from FA-1 showing

a pyritized microphytoplankton, perfectly rounded in shape, and several pyrite framboids, either isolated or forming clusters of different size. (E) Photomicrograph of a shale from FA-1 showing isolated pyrite framboids and a structured phytoclast in the central area.

Fig. 7. Field photographs of FA-2, FA-3 and FA-4. (A) Thickening upward sandstone-dominated sequences from the shoreface (FA-2) and beach face (FA-3). (B) Sandstone-dominated packages sharply separated by shale layers from FA-2 indicating progradational episodes. Sample bag is 20 X 30 cm. (C) Aspect of the sandstone and shale of the overwash zone in FA-4. Highlighted, hummocky cross-stratification (HCS) at the lower part of the interval. To the left, thin and undulating sandstone beds pinching out. Contact between FA-3 and FA-4 at the bottom right of the picture. (D) Detail of the thin and undulating sandstone beds pinching out in C.

Fig. 8. Field and microscope photographs of FA-5. (A) Shales and silicified siltstone beds from the upper part of the association unconformably overlain by Mississippian chert (Ch). (B) Tsunamite bed from the lower part of FA-5. T = tsunamite bed; S = silicified siltstone beds; Sh = black shale level. (C) Thin section normal to foliation of the tsunamite bed showing pelletoidal texture. Fine grained sandstone in pale brown and organic matter in black colour. Image obtained with crossed polars. (D) Thin section parallel to foliation of the tsunamite bed showing a conodont element. Image obtained with crossed polars. (E) Well-preserved fungal hypha from FA-5 shales.

Fig. 9. Distribution of the palynological groups through the FF Les Vilelles section with reference to facies associations. AOM = amorphous organic matter; ARL = AOM rich level. Scale bar = 1 m.

Fig. 10. Ternary diagram showing compositions of the shale samples in the Ti–Th–Hf space. AS = Average Shale (Mason, 1982); PAAS = Post-Archean Australian Shale (Taylor & McLennan, 1985); CC = Continental Crust and greywacke (Wedepohl, 1995). ARL = AOM rich level.

Fig. 11. (A) Ternary diagram of carbonate-free and apatite-free black shale samples from the FF Les Vilelles section in the A–CN–K space (adapted from Nesbitt, 2003). The apices A (Al₂O₃), CN (CaO+Na₂O) and K (K₂O) are expressed on a molar basis. (B) A–CNK–FM ternary diagram (adapted from Nesbitt, 2003) showing the main alteration trend of carbonate-free and apatite-free black shale samples, including the illite-muscovite and chlorite poles. The apices A (Al₂O₃), CNK (CaO + Na₂O+K₂O) and FM (Fe₂O₃tot+MgO) are expressed on a molar basis. CC = Continental Crust (Wedepohl, 1995); AS = Average Shale (Mason, 1982); PAAS = Post-Archean Australian Shale (Taylor & MacLennan, 1985); Pl = plagioclase; Ka = kaolinite; Chl = chlorite; Ms = muscovite; Fd = feldspar; Sm = smectite; ARL = AOM rich level.

Fig. 12. Distribution of Al-normalized element concentrations throughout the FF Les Vilelles section, indicating (in grey colour) the three identified steps of the Kellwasser event. Major and trace elements are given as weight percent ratios and element/Al₂O₃ ratios multiplied by 10⁴, respectively. ARL = AOM rich level. Scale bar = 1 m.

Fig. 13. Shale-normalized (Mason, 1982) REE spectra for shale samples from the FF Les Vilelles section. The disparate spectrum corresponds to sample KV-1 (FA-1), the sample rich in conodont skeletal elements.

Fig. 14. U versus Mo plotted in terms of enrichment factor ratios of elements from the FF Les Vilelles section. Samples from the ARL exhibit strong enrichment in these redox-sensitive elements.

Table 1. Mineral composition of selected black shale samples of the FF Les Vilelles section based on X-ray diffraction (XRD) analysis. Location of samples in Fig. 3.

Table 2. Description of the main organic components considered in this study.

Table 3. Main characteristics of the facies associations defined in this study. Scale bars in minilogs range from 1 to 45 cm.

Table 4. Geochemical composition of selected black shales from the FF Les Vilelles section. Re values are multiplied by 1000. Location of samples in Fig. 3.

Table 5. Pearson matrix of correlation coefficients between representative elements of shale samples from the FF Les Vilelles section. *Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed).

	QUARTZ	ALBITE	ILLITE	MUSCOVITE	CHLORITE
KV-26	23	6	3	51	16
KV-25	16	20	25	39	0
KV-24	20	16	0	65	0
KV-21	22	19	37	5	18
KV-20	32	9	49	2	7
KV-19	31	6	0	26	37
KV-15	5	15	30	23	27
KV-13	17	13	65	4	2
KV-10	28	14	25	9	24
KV-7	17	17	20	35	11
KV-3	27	10	12	32	20
KV-2	24	13	5	38	20

TERRESTRIAL PALYNOMORPHS	
Spores	Spores of briophytes and pteridophytes.
Equidimensional phytoclasts	Equidimensional brown and black microscopic remains of land plants.
Lath-shaped phytoclasts	Very thin brown and black microscopic remains of land plants too fragile to be preserved in moderate to high energetic settings.
Fungal hyphae	Thin, narrow, and occasionally branching filamentous structures partitioned by septa. Originally, they were part of a mycorrhiza, the symbiotic association of fungus and vascular plant roots.
MARINE PALYNOMORPHS	
Acritarchs and prasinophyceae	Cysts of marine organic-walled microphytoplankton of uncertain origin and phycmata of prasinophyte algae. Both palynological groups have been joined together in this study as they behaved in a similar manner.
UNSTRUCTURED ORGANIC MATTER	
Amorphous organic matter (AOM)	Brown to black structureless masses derived from degradation of marine and/or terrestrial organic components.

FA	LOG	MAIN CHARACTERISTICS AND OTHERS	SEDIMENTARY ENVIRONMENT AND PROCESSES
FA-5		<p>Shale dominated // No sequential pattern</p> <p>Black/dark shales with sandstone interbeds and sand/silt streaks</p> <p>Silt layers with horizontal lamination</p> <p>High proportion of continental palynomorphs including fungal hyphae and lath-shaped phytoclasts. Low proportion of marine phytoplankton and AOM</p> <p>A significant 130 cm-thick level at the upper part with high abundance of AOM and depletion of miospores and equidimensional phytoclasts (AOM rich level)</p> <p>Very weak fluorescence of OM</p> <p>Embedded at the base one wave sand level with a PHFM sequence.</p> <p>Abundant bioclasts (conodont element, homocatenids, algal oncoids and mm-scale phytoclasts). Surrounding silt layers with conodont elements and wrinkle structures</p>	<p>Lagoonal environment with swamped deposits: Lagoonal pond</p> <p>Anoxic depositional environment for the rich AOM level</p> <p>Deposition under low energy conditions, settling of fine particles and recurring subtle bottom currents</p> <p>Tsunami surge layer trapped among the lagoonal mud</p>
FA-4		<p>Heterolithic sandstone - shale association // Common soft deformation</p> <p>Minor, thin, isolated and undulated sandstone beds pinching out</p> <p>Complex sandstone packages with hummocky/swalley cross-stratification</p> <p>Shales as (1) discontinuous levels between sand beds, (2) sparse dm-thick levels, (3) thin drapes within sand beds, (4) cm-thick lenses over sand bed antinodes</p> <p>Palynomorphs as in FA-2 and FA-3 // First occurrence of fungal hyphae</p>	<p>High-energy apron deposits of the overwash zone between the shoreline sands and the coastal lagoon</p> <p>Sand storm layers trapped in mud from the coastal plain</p>
FA-3		<p>Minor climbing ripples</p> <p>Tabular or slightly undulated sandstone beds // Internal ordering: superposed horizontal sets with planar stratification // No shale drapes // Common internal erosional surfaces</p> <p>Wavy stratification // Wave ripples and micro-hummocky</p> <p>Shale levels with sand/silt streaks</p> <p>Palynomorphs proportion as in FA-2</p>	<p>Littoral environment: from upper shoreface to the ridge beach (shoreline sands)</p> <p>Increasing influence of waves and storms on the coastal seafloor</p> <p>Sandstones with planar stratification represent ridge beach deposits</p> <p>Wavy beds deposited as bed-load</p> <p>Shales represent settling of small particles from waning currents</p>
FA-2		<p>Small oscillation ripples</p> <p>Soft deformation structures</p> <p>Undulated sandstone packages with bimodal cross-lamination // Hummocky and swalley cross-stratification // Internal erosive surfaces</p> <p>Flaser and wavy bedding</p> <p>Shale layers with streak and very flattened lenses of fine sand. Frequent shale drapes</p> <p>High proportion of equidimensional phytoclasts and miospores. Microphytoplankton and lath-shaped phytoclasts present. No fungal hyphae</p> <p>Low proportion of AOM</p>	<p>Littoral environment: wave-dominated shoreface</p> <p>Depositional processes dominated by wave currents above FWB</p> <p>Well oxygenated coastal environment</p>
FA-1		<p>Shale-dominated // No sequential pattern</p> <p>Abundant AOM. Subordinate equidimensional phytoclasts, miospores and marine plankton // No lath-shaped phytoclasts or fungal hyphae recorded</p> <p>OM exudates with intense orange fluorescence</p> <p>Black shales with pyrite crystals (isolated and/or clustered in framboids) and pyritized microfossils (radiolarian and undifferentiated)</p> <p>Absence of bioturbation and current reworking evidences</p> <p>Tabular sandstone beds with horizontal lamination and graded bedding separated by erosional surfaces. Occasional undulate beds with anisotropic hummocky cross-stratification after Dumas and Arnott (2006)</p>	<p>Inner shelf below FWB</p> <p>Micro-hummocky cross-stratification after Buller & Johsen (1982) and Tinterri (2011)</p> <p>Sandstones deposited from bottom storm currents</p> <p>Shales deposited from suspension and from migration of floccule mud beds</p> <p>Intense bacterial activity</p> <p>Oxygen-deficient depositional environment</p>

SAMPLES	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	TOC	ppm																		
	Ba	Rb	Sr	Zr	Th	Nb	Y	Hf	Cr	Mo	U	V	Re*	Zn	Cu	Ni	Pb	Hg	As											
KV-27	72.3	12	4.54	0.38	1.44	0.56	2.71	0.63	0.01	0.11	0.62	253	131	69	119	10.6	16.3	24.3	3.3	80	0.5	2.61	108	5	53	169	50	43	0.08	5.6
KV-26	74.6	12	2.89	0.35	1.21	0.81	2.99	0.62	0.03	0.1	1.09	255	137	64.4	137	11.5	19.4	21.1	4.4	90	1	3.39	187	4	83	263	71	88	0.04	2.3
KV-25	59.8	10	2.08	1.8	0.36	4.12	1.09	0.53	0.005	0.06	8.52	141	53.6	124	153	8.42	12.6	28.5	4	60	14	8.4	128	2	9	30	34	207	1.57	82.9
KV-24	62.9	12	1.83	0.57	0.6	2.78	2.11	0.6	0.005	0.05	8.21	182	101	49.7	121	8.22	14	20.6	3.4	80	12	8.79	175	180	9	30	25	157	0.93	86.3
KV-23	56.7	12	1.89	0.22	0.53	2.97	2.19	0.68	0.005	0.13	13.3	203	102	57.7	132	9.87	15.7	37.5	3.8	80	15	8.72	210	38	11	22	37	213	1.54	250
KV-22	61.3	16	5.97	0.78	2.19	1.29	3.55	1	0.09	0.14	0.32	313	166	73.9	192	13.7	19.8	33.7	5.4	120	2	3.41	167	4	97	84	72	29	0.04	5.3
KV-21	80.8	8.4	3.14	0.17	1.09	0.6	1.78	0.44	0.01	0.08	0.99	164	85.3	32.4	82	7.2	10	11.7	2.3	60	1	2.24	102	2	64	150	59	16	0.02	0.6
KV-20	61.5	18	4.24	0.7	1.98	1.08	4.36	0.98	0.06	0.13	0.8	372	194	77.1	178	14.4	19.7	28.7	4.7	120	0.5	3.59	170	6	74	116	73	28	0.05	6.2
KV-19	72	13	4.24	0.2	1.59	0.54	3.14	0.64	0.01	0.07	0.12	282	149	47.3	96	10.3	14.2	19	2.7	90	0.5	1.7	108	ND	70	60	37	24	0.02	1.8
KV-15	54.9	19	5.72	1.35	2.43	1.49	4.36	1.05	0.2	0.21	0.94	385	193	82.8	196	17.1	30.7	36	5.3	120	0.5	2.9	220	6	82	442	75	16	0.06	7.8
KV-13	62.9	16	3.43	1.26	1.66	2.22	3.35	0.91	0.15	0.14	0.81	305	155	82.1	196	15.1	20.6	31.9	5.6	120	2	3.98	177	10	110	186	56	15	0.31	15.4
KV-12	60.1	17	4.18	1.16	2.02	1.8	3.82	0.98	0.16	0.13	0.4	327	176	83.2	177	14.6	19.3	31.8	5	140	2	3.05	166	3	134	72	47	23	0.02	2.7
KV-11	64.8	14	6.02	1.19	2.22	1.71	2.55	0.9	0.12	0.2	0.17	248	112	77.3	214	13	17.9	35.9	6	100	0.5	2.67	111	ND	66	79	45	7	0.02	1.8
KV-10	62.1	17	3.45	0.52	1.7	1.53	3.97	0.99	0.05	0.12	1.29	376	185	82.4	232	15.9	22.8	32.9	6.3	120	0.5	4.32	177	11	86	216	75	42	0.39	18.2
KV-9	59	20	4.48	0.81	2.27	0.97	4.86	0.99	0.08	0.13	0.16	373	227	71.6	163	14.4	20.2	33.4	4.6	150	2	2.71	176	ND	99	56	38	38	0.01	1.3
KV-8	61.6	19	4.42	0.75	2.17	0.95	4.73	1.05	0.08	0.12	0.12	369	221	65.6	205	15.8	21.4	33.6	5.8	140	2	2.28	160	ND	81	34	37	12	0.03	1.2
KV-7	55.7	20	5.03	0.92	2.43	0.79	5.08	0.96	0.11	0.09	0.23	421	228	71.5	149	14	19.4	27.7	4.3	130	0.5	2.23	178	ND	85	100	48	6	0.07	1.1
KV-6	58.5	18	6.41	1.76	2.84	0.99	4.11	1	0.23	0.13	0.14	349	196	83.5	168	14.9	19.9	35.6	4.8	150	2	2.29	167	ND	97	40	46	13	0.04	1.6
KV-5	60	15	6.49	0.18	1.38	0.82	2.58	0.87	0.01	0.52	2.8	291	123	58.7	213	13.8	19	22.4	5.8	90	1	6.6	210	19	64	167	64	55	0.34	25
KV-4	55.5	21	5.03	0.08	1.54	0.56	4.06	0.98	0.01	0.16	0.4	440	201	94.9	203	16.8	22	21.5	5.5	120	0.5	3.44	161	ND	79	81	24	18	0.07	4.5
KV-3	47.7	12	7.06	12.1	1.63	0.22	1.54	0.37	0.02	9.71	0.58	199	84.9	248	95	10.7	14.2	34.7	2.8	50	0.5	14.8	94	8	96	92	37	21	0.05	1
KV-2	61	18	5.9	0.28	1.58	0.39	3.34	0.79	0.01	0.36	1.08	381	168	89.8	126	13.1	18.7	24.8	3.5	100	0.5	2.81	138	4	97	112	46	16	0.08	3.1
KV-1	65	16	3.19	0.05	1.04	0.9	2.94	0.94	0.01	0.35	2.73	350	144	62.4	223	15.2	21.5	24.1	15	100	1	7.7	235	21	27	109	41	39	0.32	16.4
Al ₂ O ₃ NORMALIZED																														
KV-27	6.08	1	0.38	0.03	0.12	0.05	0.23	0.053	0.001	0.01	0.05	21.3	11	5.8	10	0.89	1.37	2.04	0.3	6.72	0.04	0.22	9	0.42	4.45	14.2	4.2	3.6	0.01	0.47
KV-26	6.19	1	0.24	0.03	0.1	0.07	0.25	0.051	0.002	0.01	0.09	21.2	11.3	5.34	11.4	0.95	1.61	1.75	0.4	7.47	0.08	0.28	16	0.332	6.89	21.8	5.9	7.3	0	0.19
KV-25	5.86	1	0.2	0.18	0.04	0.4	0.11	0.052	0.000	0.01	0.84	13.8	5.25	12.1	15	0.83	1.24	2.79	0.4	5.88	1.37	0.82	13	0.196	0.88	2.94	3.3	20	0.15	8.13
KV-24	5.45	1	0.16	0.05	0.05	0.24	0.18	0.052	0.000	0	0.71	15.7	8.74	4.3	10.5	0.71	1.21	1.78	0.3	6.93	1.04	0.76	15	15.58	0.78	2.6	2.2	14	0.08	7.47
KV-23	4.81	1	0.16	0.02	0.04	0.25	0.19	0.058	0.000	0.01	1.13	17.2	8.6	4.89	11.2	0.84	1.33	3.18	0.3	6.78	1.27	0.74	18	3.22	0.93	1.86	3.1	18	0.13	21.2
KV-22	3.74	1	0.36	0.05	0.13	0.08	0.22	0.061	0.005	0.01	0.02	19.1	10.1	4.51	11.7	0.83	1.21	2.05	0.3	7.32	0.12	0.21	10	0.244	5.91	5.12	4.4	1.8	0	0.32
KV-21	9.57	1	0.37	0.02	0.13	0.07	0.21	0.052	0.001	0.01	0.12	19.4	10.1	3.84	9.72	0.85	1.18	1.39	0.3	7.11	0.12	0.27	12	0.237	7.58	17.8	7	1.9	0	0.07
KV-20	3.44	1	0.24	0.04	0.11	0.06	0.24	0.055	0.003	0.01	0.04	20.8	10.8	4.31	9.94	0.8	1.1	1.6	0.3	6.7	0.03	0.2	9	0.335	4.13	6.48	4.1	1.6	0	0.35
KV-19	5.45	1	0.32	0.02	0.12	0.04	0.24	0.048	0.001	0.01	0.01	21.4	11.3	3.58	7.27	0.78	1.08	1.44	0.2	6.82	0.04	0.13	8	ND	5.3	4.55	2.8	1.8	0	0.14
KV-15	2.86	1	0.3	0.07	0.13	0.08	0.23	0.055	0.010	0.01	0.05	20.1	10.1	4.31	10.2	0.89	1.6	1.88	0.3	6.25	0.03	0.15	11	0.313	4.27	23	3.9	0.8	0	0.41
KV-13	3.98	1	0.22	0.08	0.11	0.14	0.21	0.058	0.009	0.01	0.05	19.3	9.81	5.2	12.4	0.95	1.3	2.02	0.4	7.59	0.13	0.25	11	0.633	6.96	11.8	3.5	0.9	0.02	0.97
KV-12	3.47	1	0.24	0.07	0.12	0.1	0.22	0.057	0.009	0.01	0.02	18.9	10.1	4.81	10.2	0.84	1.12	1.84	0.3	8.09	0.12	0.18	10	0.173	7.75	4.16	2.7	1.3	0	0.16
KV-11	4.58	1	0.43	0.08	0.16	0.12	0.18	0.064	0.008	0.01	0.01	17.5	7.92	5.46	15.1	0.92	1.27	2.54	0.4	7.07	0.04	0.19	8	ND	4.66	5.58	3.2	0.5	0	0.13
KV-10	3.7	1	0.21	0.03	0.1	0.09	0.24	0.059	0.003	0.01	0.08	22.4	11	4.9	13.8	0.95	1.36	1.96	0.4	7.14	0.03	0.26	11	0.655	5.12	12.9	4.5	2.5	0.02	1.08
KV-9	3.02	1	0.23	0.04	0.12	0.05	0.25	0.051	0.004	0.01	0.01	19.1	11.6	3.66	8.34	0.74	1.03	1.71	0.2	7.67	0.1	0.14	9	ND	5.06	2.86	1.9	1.9	0	0.07
KV-8	3.33	1	0.24	0.04	0.12	0.05	0.26	0.057	0.004	0.01	0.01	19.9	11.9	3.55	11.1	0.85	1.16	1.82	0.3	7.57	0.11	0.12	9	ND	4.38	1.84	2	0.6	0	0.06
KV-7	2.74	1	0.25	0.05	0.12	0.04	0.25	0.047	0.005	0	0.01	20.7	11.2	3.52	7.34	0.69	0.96	1.36	0.2	6.4	0.02	0.11	9	ND	4.19	4.93	2.4	0.3	0	0.05
KV-6	3.26	1	0.36	0.1	0.16	0.06	0.23	0.056	0.013	0.01	0.01	19.4	10.9	4.65	9.36	0.83	1.11	1.98	0.3	8.36	0.11	0.13	9	ND	5.4	2.23	2.6	0.7	0	0.09
KV-5	4	1	0.43	0.01	0.09	0.05	0.17	0.058	0.001	0.03	0.19	19.4	8.17	3.91	14.2	0.92	1.27	1.49	0.4	6	0.07	0.44	14	1.267	4.27	11.1	4.3	3.7	0.02	1.67
KV-4	2.62	1	0.24	0	0.07	0.03	0.19	0.046	0.000	0.01	0.02	20.8	9.48	4.48	9.58	0.79	1.04	1.01	0.3	5.66	0.02	0.16	8	ND	3.73	3.82	1.1	0.8	0	0.21
KV-3	3.94	1	0.58	1	0.13	0.02	0.13	0.031	0.002	0.8	0.05	16.4	7.02	20.5	7.85	0.88	1.17	28.7	0.2	4.13	0.04	1.22	8	0.661	7.93	7.6	3.1	1.7	0	0.08
KV-2	3.38	1	0.33	0.02	0.09	0.02	0.19	0.044	0.001	0.02	0.06	21.1	9.28	4.98	6.98	0.72	1.04	1.37	0.2	5.54	0.03	0.16	8	0.222	5.37	6.2	2.5	0.9	0	0.17
KV-1	4.17	1	0.2	0																										

















