Geological Quarterly, 2004, **48** (4): 323–332

Late Devonian facies variety in Iran: volcanism as a possible trigger of the environmental perturbation near the Frasnian-Famennian boundary

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Mahmudy Gharaie M. H., Matsumoto R., Kakuwa Y. and Milroy P. G. (2004) — Late Devonian facies variety in Iran: volcanism as a possible trigger of the environmental perturbation near the Frasnian-Famennian boundary. Geol. Quart., **48** (4): 323–332. Warszawa.

Upper Devonian successions surrounding the Frasnian-Famennian (F-F) boundary in Iran consist of mixed carbonate/silisiclastic deposits. The successions are characterized by conspicuous ferruginous limestones, clay-rich units, black shales, and mafic volcanic rocks that provide important insights into palaeoenvironmental conditions during this interval of Earth's history. An increase of kaolinite/illite ratio in clays associated with the F-F boundary suggests that increased chemical weathering was facilitated by warm and humid climatic conditions. Distinctive ferruginous-oolite deposits overlying the crucial Frasnian-Famennian boundary interval indicate a high supply rate of Fe-bearing clay originated during enhanced weathering under such climatic conditions. Black shales associated with the F-F boundary are interpreted to be the result of a high primary productivity caused by an increased influx of land-derived nutrients and regional volcanic activity. Widespread rift-related, basaltic activity along eastern Laurussia and northern Gondwana during the mid-Late Devonian is believed to have contribution to this global warming surrounding the F-F boundary.

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Key words: Frasnian-Famennian boundary, Iran, black shale, ironstone, greenhouse, volcanism.

INTRODUCTION

The Late Devonian represents an important environmental change in the Earth's history, particularly the mass extinction in the latest Frasnian (see review in McGhee, 1996). Conodont-based biostratigraphy has been thoroughly established (Sandberg *et al.*, 1988), and the critical facies change has been well described, especially in low-latitude carbonate domains in Europe, North America, Australia and South China (e.g. Buggisch, 1991; Schindler, 1993; Becker and House, 1994; Claeys *et al.*, 1996; McGhee, 1996; Walliser, 1996; Chen *et al.*, 2002; Racki *et al.*, 2002).

During the Late Devonian Iran was situated on the northern margin of Gondwana in the southern hemisphere at a latitude close to 30°S (Scotese and McKerrow, 1990; Stampfli *et al.*, 2002), facing the semi-restricted Palaeotethys Ocean to the north. Devonian deposits are widely distributed in Iran (Huckriede *et al.*, 1962; Gaetani, 1965; Stöcklin *et al.*, 1965; Davodzadeh and Weber, 1987; Ghavidel-Syooki, 1994; Dastanpour, 1996; Ashouri, 1997; Wendt *et al.*, 1997, 2002; Yazdi, 1999, 2001; Hairapetian and Yazdi, 2003). The exact position of Frasnian-Famennian (F-F) boundary has not been clearly defined because of a predominance of a shallow-water conodont biofacies that have proven inadequate for precise age determinations. However, concept of the key stage-boundary interval, spanning the uppermost Frasnian to lowermost Famennian is based on conodont biostratigraphy in the reference Howz-e-Dorah section in Central Iran (Ashouri, 1997; Wendt *et al.*, 1997; Yazdi, 1999, 2001), i.e. the main phase of the Kellwasser (KW) Crisis (as defined by Schindler, 1993). As shown by the cited reports on various Iranian successions, sea level fluctuated between the lower subtidal and peritidal. The presumed F-F transition is characterized by dark gray to black shale in some sections, indicating Kellwasser transgressive-anoxic event in Iran, as proposed by Walliser (1996, p. 233). However, the recognition of this anoxic facies in Iran has not been confirmed (see Wendt *et al.*, 2002) until now.

The purpose of this paper is to present the results of an integrated sedimentological and geochemical study of a variety of widely exposed Upper Devonian lithofacies (carbonate iron-

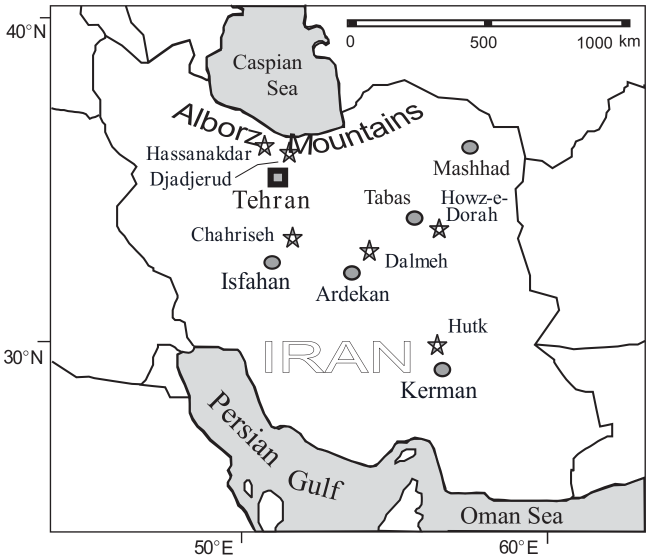


Fig. 1. Section localities in Iran (shown by stars)

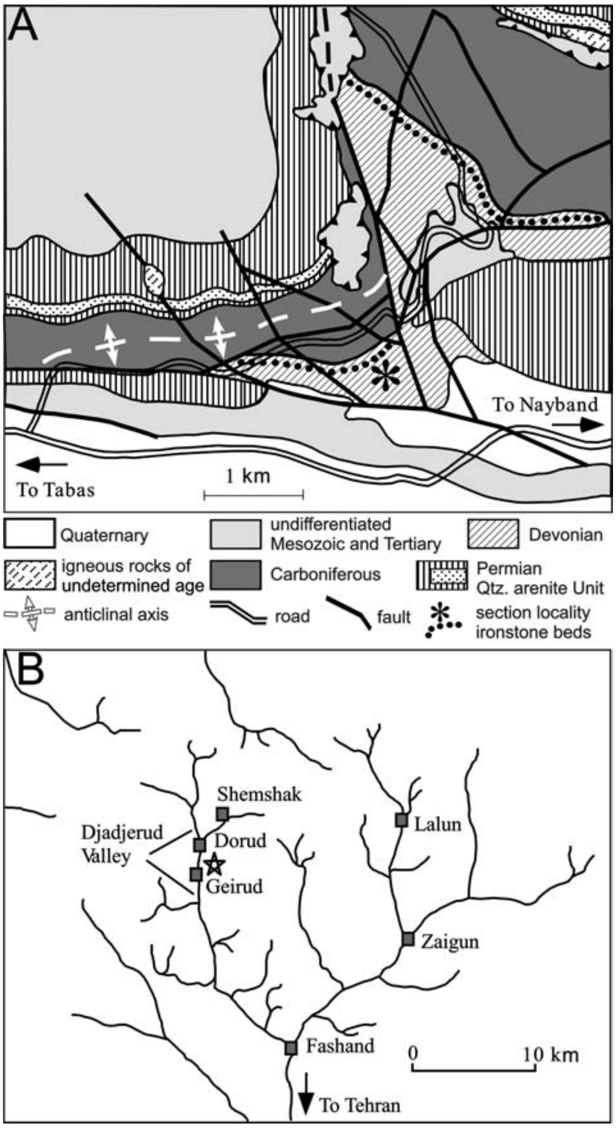


Fig. 2. A — geological map of Howz-e-Dorah area, east of Tabas (revised after Yazdi, 1999) with the location of studied section; B — sketch map of Djadjerud Valley with the location of Geirud section (shown by star)

stones, ferruginous units, and firstly described black shales) from Central Iran (Fig. 1 and 2A) in order to provide new insights into palaeoenvironmental conditions related to the F-F boundary. In addition, a preliminary insight into basaltic horizons in Northern Iran (Mahmudy Gharaie *et al.*, in prep.), combined with regional comparisons, allows us to tentatively propose a causal link between volcanic activity and the mid-Late Devonian global change.

SAMPLING AND METHODS

Ironstone samples were examined from the Howz-e-Dorah section (Stöcklin *et al.*, 1965) in Central Iran. The internal fabric in ferruginous grains of ironstones was examined under both transmitted and reflected light in binocular microscope. Selected bulk samples of twenty seven ferruginous carbonates, forty three siliciclastics, and seventeen volcanic rocks were analyzed by X-ray powder diffractometer (*XRD*) at the University of Tokyo to examine the mineral composition. Separation of the fine fraction of siliciclastic particles was conducted to determine the clay mineral composition and its secular and spatial variations in clay-rich sandstones of the Howz-e-Dorah section. Ferruginous grains in polished thin sections of the ironstones were analyzed by electron microprobe using a *JEOL-JXA-8900L* for selected major elemental constituents, expressed as oxides such as SiO_2, Al_2O_3, FeO and CaO. Concentrations of trace and rare earth elements in the samples were determined by ICP-MS measurement (*HP4500 ICP-MS*). Total organic carbon (TOC), an important component of black shale, was measured for the purpose of a palaeoenvironmental interpretation in 43 sand-siltstone and shale samples, by carbon determinator (*LECO CNS 2000*) in the University of Tokyo.

GEOLOGICAL SETTING

Howz-e-Dorah section (Fig. 2A) is located at the southern end of Shotori Range, 45 km SE of Tabas, Central Iran. This is one of the best-known Upper Devonian sections in Iran (Stöcklin *et al.*, 1965; Alavi-Naini, 1993; Ashouri, 1997; Wendt *et al.*, 1997; Yazdi, 1999, 2001) and represents the Shishtu Formation, late Frasnian to early Tournasian in age (Fig. 3). The lower part of the Shishtu Formation (Stöcklin *et al.*, 1965) includes mostly peritidal carbonates, characterized by well-bedded grey wackestone, packstone and grainstone intercalated with siltstone and claystone. The limestone beds decrease in thickness upward and there is a change to siliciclastic-dominated facies. Approximately 4 m thick black shale, at around the Frasnian-Famennian boundary, overlies the siliciclastic unit and passes up into a ferruginous unit of 25 m thick. The shaly unit is here firstly described in the Shotori Range, as the section studied by Yazdi (1999; fig. 3) is located about 3 kilometers northward where the crucial interval is rather poorly exposed. The siltstone and black shale unit in

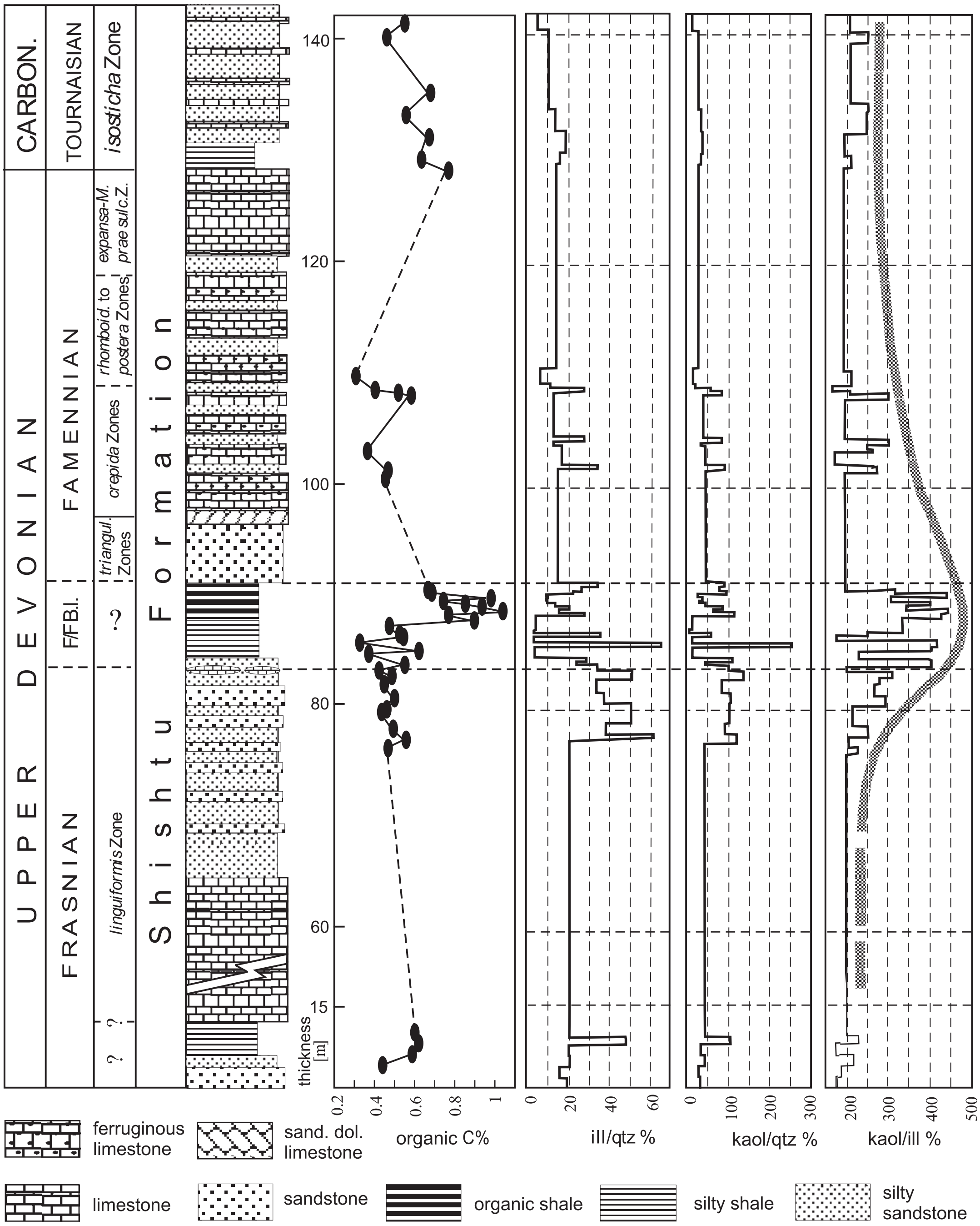


Fig. 3. Stratigraphy, organic carbon content and clay mineralogy in Howz-e-Dorah section

High organic carbon content ranging from 0.7 to 1.1%, characterizes black shale in the interval of the Frasnian-Famennian boundary (F/F B.I.); note that the clay to quartz and kaolinite to illite ratios are on average higher near F-F boundary interval than other measured Frasnian and Famennian values; conodont zonation is after Yazdi (1999); qtz — quartz, kaol — kaolinite, ill — illite

Howz-e-Dorah section overlies a placoderm-bearing limestone, which is well-exposed in the Shotori Range and suggest the sections are correlative.

Position of the key boundary, was established by Yazdi (1999) with reference to the disappearance of ancyrodellids (*A. nodosa*, late *A. curvata*) within assumed interval of the *linguiformis* Zone. This is a positive exception among the Iranian F-F successions, characterized by biostratigraphically non-diagnostic shallow-water polygnathid-icriodid faunas (with *Icriodus alternatus alternatus*), and last occurrence of tentaculitids and/or brachiopod data are therefore helpful in determination of the key boundary level (Yazdi, 2001; Dastanpour and Aftabi, 2002; Wendt *et al.*, 2002; Hairapetian and Yazdi, 2003). Also in the Howz-e-Dorah section, upper Frasnian conodont zones from Early *rhenana* Zone remain mostly undivided, and the basal Famennian *triangularis* Zone is only ambiguously identified by Yazdi (1999). The well-bedded reddish limestones correspond certainly to the *crepida* Zone of the Famennian stage

(Fig. 3). The distinctive ferruginous succession is overlain by Tournaisian dark gray shales and sandstones with thin limestone beds intercalations (Wendt *et al.*, 1997; Yazdi, 1999, 2001).

SELECTED LITHOFACIES

Sedimentological facies analysis of distinctive lithofacies, associated with the F-F boundary in Central Iran is used to provide important palaeoenvironmental information on the Late Devonian events.

BLACK SHALE

Organic-rich, black shales (3–4 m thick), associated with the F-F boundary interval, are widely correlateable in Central Iran, as demonstrated by Hutk and Gazestan sections (Wendt *et al.*, 2002, figs. 5–6; see also Matsumoto *et al.*, 2002, fig. 2) in the Kerman area, ~ 350 km southward of Howz-e-Dorah section, as well as in the Chahriseh section in Kaftari Mountain, Isfahan area (Dr. M. A. Jafarian, pers. comm.). The total organic carbon content (TOC) of the black shale ranges from 0.7 to 1.1 . This is higher than 0.65% typical for the average shale values (Vine and Tourtelot, 1970) and indicates that the rock represents “black shale”, according to the definition by Huyck (1990). Benthic organisms are generally absent, but small brachiopod shell molds (~ 1 cm in diameter) are sparsely visible in bedding surfaces. Hand specimens of the shales are characterized by planar parallel lamination (< 5 mm thick laminae). Thin-sections show micro-laminae between 1 to 2 mm thick. Chemical analysis and X-ray diffractometry indicate that the shale is non-carbonate. The constituent clay minerals are kaolinite and illite, with a kaolinite to illite ratio of three to four.

FERRUGINOUS-OOLITE LITHOFACIES

This unit is ~25 m thick and well exposed in Howz-e-Dorah area. Abundant ferruginous ooids occur in limestone beds named as “Cephalopod Beds” (Stöcklin *et al.*, 1965). In other regions of Central Iran, Famennian ferruginous deposits of a similar age or stratigraphic position are developed in carbonate (Hutk, Dalmeh) or sandy (Chahriseh) facies (Mahmudy Gharaie, 2000; Yazdi, 2001; Matsumoto *et al.*, 2002). The individual ooid grains with the predominant size ranging from 300 to 700 µm consist of nuclei enveloped by a concentrically laminated cortex (Fig. 4) composed of hematite, goethite and minor amount of kaolinite and chlorite. Marine bioclasts, ferruginous aggregates, broken ferruginous ooids and lithoclasts serve as nuclei for the ooids and support a fully marine origin for the grains. EPMA examination of the ooids indicates that they are composed of continuous laminae of hematite and silicate.

Fine ferruginous particles are normally transported to a near-shore environment either as pedogenetically formed colloids derived from ancient soil horizons (Siehl and Thein, 1989), or as a coating of clay particles (Harder, 1989). Some of the examined Devonian ooids have an oblate, ellipsoid shape (Fig. 4). Such ferric oxide ooids are probably too rigid and brittle to have been formed by deformation of spherical ooids (Hal-

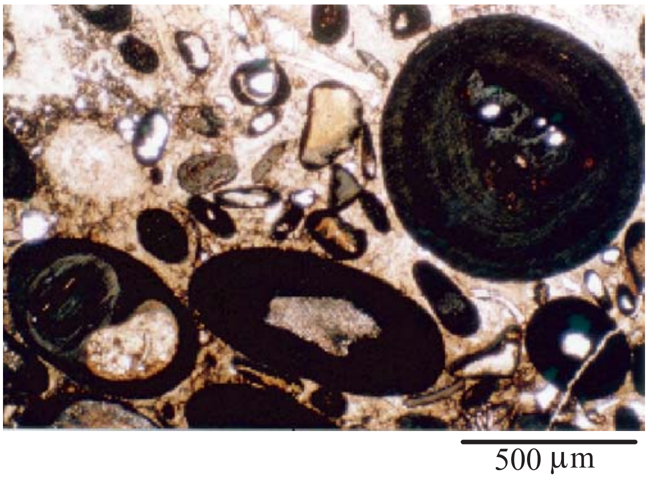


Fig. 4. Ferruginous grains in examined Famennian ironstones from the Howz-e-Dorah section (Fig. 3); the shell fragments as nuclei in some grains coated by concentric layers of the ferruginous cortex

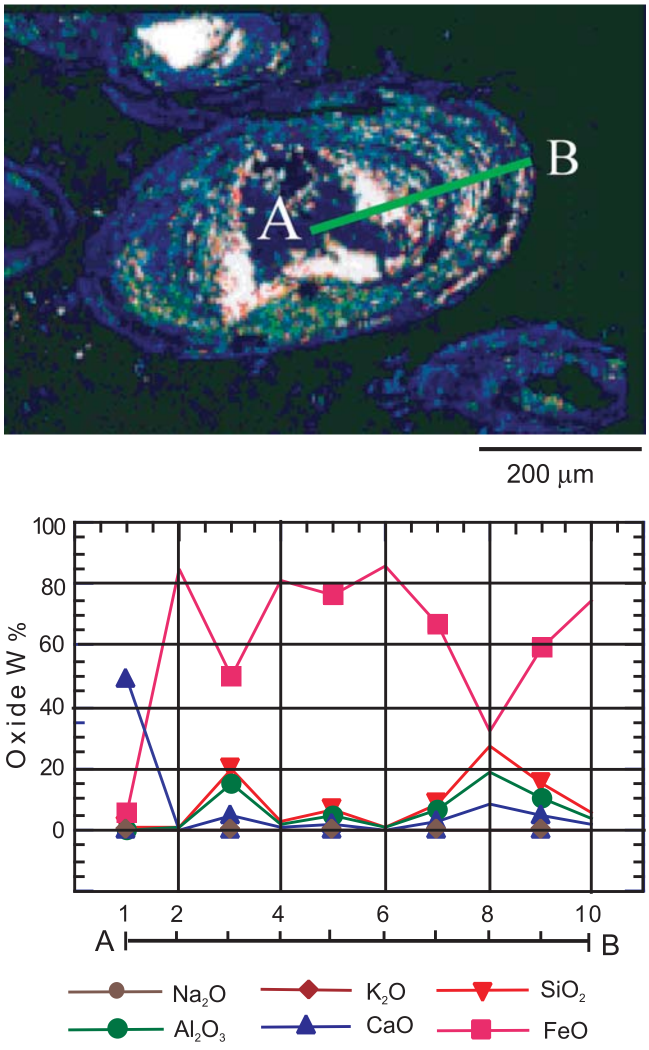


Fig. 5. EPMA scanned microphotograph and point analysis for determination of major oxides in cortex and nuclei in ferruginous grains of oolitic ironstone. Microphotograph shows distribution of Al in the grain. Ten point data from A to B represent the geochemical composition indicating aluminosilicates as main component. The core (point no. 1) contains higher CaO than cortex but no other oxides except for a few percent of FeO, indicating carbonate and probably a calcite shell fragment as nuclei

lam, 1975; Dreesen, 1989). However, Guerrak (1987) has demonstrated that clay mineral ooids are sufficiently plastic to deform into ellipsoid shapes from burial compaction. This suggests the concentric precipitation of iron and clay materials around nuclei is a primary feature of the grains. Electron microprobe analysis demonstrates that the soluble elements in clays such as Ca, Mg, Na, K *etc*. were weathered or transported out after the accretion on nuclei, leaving residual Si and Al. In the cortex of the ooid, an irregular part of opaque ferric oxide exhibits the relative abundance of iron, silica and aluminum shown in Figure 5. The concentric fabric of the ferruginous ooids probably originated by mechanical accretion of suspended particulate matter, such as hydrated iron oxides and detrital clay minerals, around a nucleus.

Similar lithofacies have also been documented from the contemporaneous Upper Devonian successions in other parts of the world including North Africa (Northern Gondwana; van Huten and Karasek, 1981) and Western Europe (Laurussia), where five ironstone horizons from *crepida* to early *marginifera* zones were reported by Dreesen (1989).

SILICICLASTIC FACIES AND KAOLINITE/ ILLITE RATIO

A 37 meter thick siliciclastic unit in the middle part of Howz-e-Dorah section ranges from the *linguiformis* to *triangularis* Zones (Fig. 3). This unit is overlain by the ferruginous carbonate rocks (cephalopod limestone) intercalated with siltstones, silty sandstones and sandstones. The interbedded sandstones are mainly arkoses with clay-rich matrix. The clay minerals largely comprise kaolinite and illite. Stratigraphic variations of clay minerals and the ratios of clay minerals and quartz are shown in Figure 3. Kaolinite and illite show an increased abundance in the rocks of the F-F boundary interval in comparison to the lower and upper parts of the succession. The high kaolinite/quartz ratios are conspicuous from the F-F boundary passage to the lower Famennian. The kaolinite/illite ratio shows a more striking stratigraphic variation with ratios increasing in the terminal Frasnian and decreasing in the upper Famennian, suggesting a major change in the provenance.

LATE DEVONIAN BASALT VOLCANISM IN IRAN

Although there is not any recognized volcanic record in the Howz-e-Dorah section in Central Iran, several thick and distinctive basalt horizons have been documented from the Upper Devonian of Alborz Mountain Range in northern Iran (Assereto, 1963; Alavi-Naini, 1993; Alavi, 1996). Upper Devonian basalts in north Iran largely consist of lava flows, locally with pillow structures. Thick horizons of basalt are found in central Alborz (Gaetani, 1965; Wensink *et al.*, 1978; Alavi-Naini, 1993). The less extensive lava flows and other volcanic activity signatures have been reported from other regions such as Azerbaijan province in northwestern Iran (Alavi and Bolourchi, 1973), the Binalud Mountains (Lammerer *et al.*, 1984) and Aghdarband (Ruttner, 1991) in northeastern Iran. However, the dating of this volcanism is not well constrained in these localities, and some of them could be even post-Devonian in age (Wendt *et al.,* 2002).

Basalt horizons from the Djadjerud Valley in the southern part of Central Alborz, about 40 km north-east of Tehran (Figs. 1 and 2B), occur in the Geirud Formation (Assereto, 1963), which is characterized by fossiliferous carbonate and siliciclastic rocks with intercalated mafic volcanics (Stampfli *et al.*, 1991; Alavi, 1996). Two distinctive basalt horizons consisting of lava flow, locally exhibiting pillow structures, are exposed over a lateral distance of about 25 km. The upper volcanic horizon (~ 120 m thick) overlies the upper Famennian plant fossils-bearing beds (Gaetani, 1965; Wensink *et al.*, 1978). The thinner lower basalt (~ 45 m) is emplaced on the top of the brachiopod-rich (i.e., *Ptychomaltoechia elburzensis* Zone) limestone beds, for which an upper Frasnian–lower Famennian stratigraphic position has been proposed by Gaetani (1965). Dashtban (1996) documented *Rhinodipterous* fish remains in the fosiliferous limestone below the lower basalt horizon and correlated them in Lalun, Zagun and Djadjerud sections in Central Alborz. Similar fish remains have already been documented only in Frasnian formations in Kerman region, southeastern Iran (Janvier, 1974, 1981; Dashtban, 1996), and the Frasnian age

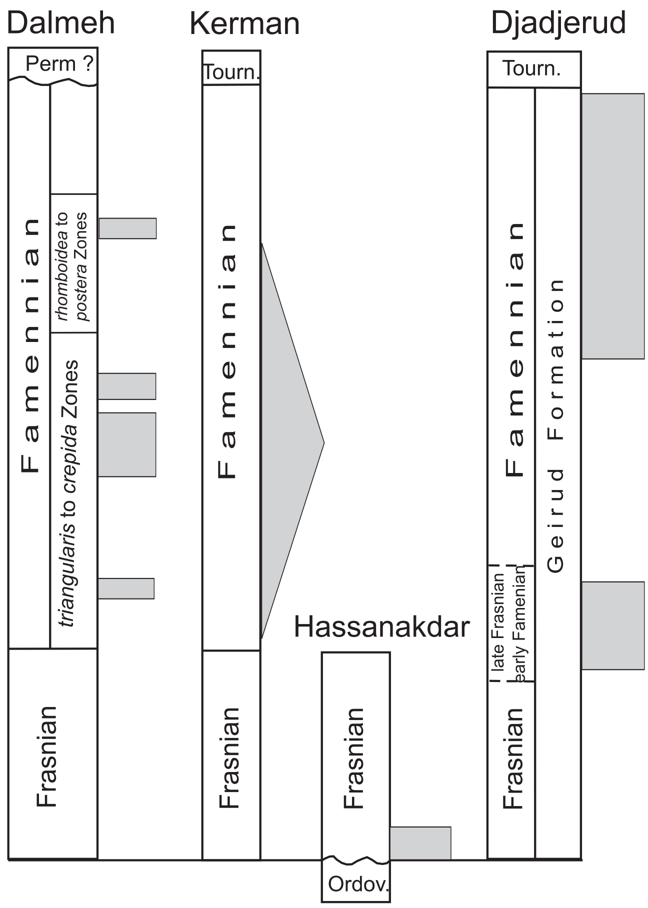


Fig. 6. Timing of basalt units in selected Iranian sections (see Fig. 1): central Iran, Ardekan area (conodont biostratigraphy after Hairapetian and Yazdi, 2003, fig. 3); southeastern Iran, Kerman area (after Wendt *et al*., 2002, fig. 4, Zone C); northern Iran, Central Alborz, Hassanakdar area (dated by palynomorphs, after Ghavidel-Syooki, 1994, fig. 2); northern Iran, Central Alborz, Djadjerud Valley (Mahmudy Gharaie, 2002)

has also been proposed for the equivalent limestone beds in Geirud Formation by Partoazar *et al.* (2002). Thus, the lower lava flow is enveloped by the Frasnian and Famennian sedimentary rocks suggesting its late Frasnian to early Famennian timing (Fig. 6, Djadjeroud section). The Geirud Formation basalt is characterized by subophitic and porphyritic texture with euhedral to subhedral olivine, clinopyroxene and plagioclase phenocrysts in a groundmass of plagioclase laths. In addition to the major constituents, the mafic volcanic rock also contains subordinate serpentine, calcite and chlorite. Discriminative diagrams, such as Ti/Y versus Nb/Y and Ti/Zr, strongly indicate that the basalt belongs to an intra-plate volcanic variety (Mahmudy Gharaie, 2002).

In the Kerman area, Wendt *et al.* (2002) have also noted igneous activity in early Famennian (Fig. 6, Kerman section), although this supposition is supported only by 1 m thick basalt in the undivided Upper Devonian carbonates at the Kereshk section (Wendt *et al*., 2002, fig. 10). However, more conclusive evidence of volcanic activity is evident from 3 of 4 thicker Famennian volcanic horizons, including the thickest one up to 10 m, within conodont-dated limestones of the *triangularis* to *crepida* zones in the Dalmeh section near Ardekan in Central Iran (Fig. 6, Dalmeh section). The above evidence suggests that intra-plate eruptive activity surrounding the Frasnian-Famennian interval in different parts of the Iran plate can be reasonably assumed (Fig. 6), however, the precise dating of these events is required.

ENVIRONMENTAL INTERPRETATION OF KEY SEDIMENTARY UNITS

BLACK SHALE AS A RECORD OF HIGHLY PRODUCTIVE, ANOXIC OCEAN

Widespread black shale deposition in the latest Frasnian is considered an equivalent to the upper Kellwasser horizon typical of the Frasnian-Famennian boundary event (Buggisch, 1991; Schindler, 1993; Walliser, 1996). Organic-rich black shale deposition requires a high influx of organic matter and/or conditions conductive for its preservation, especially depletion of dissolved oxygen in water above the sediment/water interface (Arthur and Sageman, 1994). Bulk sedimentation rate is another factor in preservation of organic matter (Emerson Hedges, 1988). Marine transgression is the most common interpretation for the black shale caused by the rise of oxygen minimum zone (OMZ; e.g. Hallam and Bradshaw, 1979; Eder and Franke, 1982; Geldsetzer, 1988; Arthur and Sageman, 1994; Lüning *et al*., 2004). The relatively low TOC of the organic carbon-rich shale in Central Iran (Fig. 3), in comparison with an average "black shale", may suggests that the high organic productivity scenario for the black shale deposition is not relevant for this unit. However, the bulk sedimentation rate of the black shale is not well understood: the clastic dilution by siliciclastic materials, as well as reduced organic matter preservation in conditions of somewhat fluctuating bottom water oxygenation (see examples in Racki *et al.*, 2002) might have resulted in the low TOC of the Iranian black shale. Thus, a high primary productivity model is in general feasible for the KW-type deposition, according to Joachimski *et al.* (2001) and Godderis and Joachimski (2004).

The upper Frasnian black shales of the two Kellwasser horizons are usually linked with rapid sea level rises (Sandberg *et al*., 1988; Schindler, 1993). The anoxia may have been caused by the encroachment of the OMZ upon epicontinental areas during this transgressive pulse (e.g. Claeys *et al*., 1996; Lüning *et al*., 2004). The rise of OMZ is thus thought to have close genetic relation with the transgression and the high primary organic productivity.

CLAY MINERAL INDICES AS AN EVIDENCE OF ENHANCED CHEMICAL WEATHERING

The use of clay minerals in marine sediments as a palaeoclimatic proxy for adjacent continents has been promoted based on the chemical and mechanical weathering sequence of crystalline rocks in various environments (Paquet, 1970; Parrish, 1998). Clay assemblages dominated by illite are indicative of low intensity of chemical weathering (Singer, 1984). Kaolinite, on the other hand, is the product of chemical weathering and the most reliable indicator for a palaeoclimate determination (Parrish, 1998). The ratio of kaolinite to illite is called as "clay mineral index", and the high abundance of kaolinite relative to illite suggests intensified chemical weathering (Robert and Kennet, 1994, 1997). Based on this assumption the gradual increase of the kaolinite/illite ratio, which started in the terminal Frasnian, indicates the climate change from less to more humid and warmer conditions in that time. The high abundance of kaolinite relative to illite (Fig. 3), and decrease of the ratio indicates that the climate warming persisted into the early Famennian only.

HIGH FLUX OF IRON-BEARING CLAYS TO CONSTITUTE IRONSTONE

The concentration of iron-rich clay minerals in ooids strongly indicates the influx of iron and clay into the shallow marine environment during the early Famennian. Two possible sources are proposed for iron-bearing gel-like alumino-silicates (van Huten, 1985; Sturesson, 1992, 1995; Garzanti, 1993; Heikoop *et al.*, 1996; Sturesson *et al.*, 2000), which may be directly or indirectly related to the mid-Late Devonian environmental change:

1. Increased chemical weathering of feldspar-rich rocks of adjacent landmass and transportation of Fe-rich clays to the marine basin. Increased chemical weathering processes were probably the result of climate change to warmer and more humid conditions, or may have been induced by adequate soil-air CO_2 pressure maintained by elevated atmospheric pCO_2 levels.

2. Influx of volcanic ash into shallow marine settings and the accretion of clay size aluminosilicates to the cortex of ooid grains, what implies an explosive eruption. However, the seawater enrichment in Fe, Al and Si could have also resulted from hydrothermal fluids and/or rapid weathering of fresh volcanic rocks (Sturesson *et al.*, 2000).

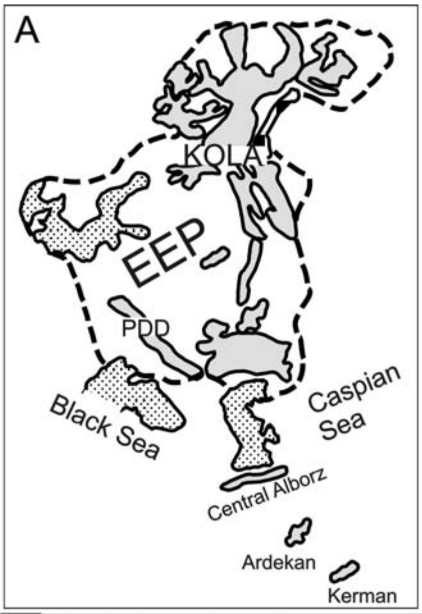
BASALT VOLCANISM AS A TRIGGER OF GLOBAL WARMING

Regional volcanism would have increased atmospheric CO_2 concentration thereby contributing to the long-term global climatic warming (Wignall, 2001), as suggested for the Kellwasser Crisis by Buggisch (1991) and Becker and House (1994). Volcanism in Northern Iran appears to have been a part of a much larger Late Devonian igneous province in the Palaeotethys Ocean peripheries (Mahmudy Gharaie, 2002). This diverse magmatism is best known from the East European Platform (EEP; Fig. 7A), which includes one of the world's largest alkaline massifs comprising 25 magmatic centers within an area of 100 000 km^2 (Kola Province, Wilson and Lyashkevich, 1996). The Pripyat-Dnepr-Donets rift system is more than 800 km long and separates the Ukrainian Shield from the Voronezh Massif (Kusznir *et al*., 1996). Major, trace elements and Sr-Nd isotopic studies indicate that the volcanism is related to the most primitive basic and ultrabasic magmas (Wilson and Lyashkevich, 1996). Estimates of the amount of extension and the chemical characteristics of magma strongly suggest that the Late Devonian magmatism was triggered by an upwelling of a thermally and geochemically anomalous mantle. Rift related volcanism and domal basement uplift were contemporaneous at several localities over vast areas of EEP (e.g. Wilson and Lyashkevich, 1996; Yudina *et al.*, 2002). This suggests that the thermal and geodynamic evolution of the eastern Laurussia could have been influenced by a cluster of mantle plumes (Wilson and Lyashkevich, 1996; the superplume event 7 sensu Abbott and Isley, 2002). Additional evidence of rift-related volcanism surrounding the F-F boundary interval has been documented from Siberia and South China (e.g., Racki, 1998; Veimarn *et al.*, 1998; Abbott and Isley, 2002; Ma and Bai, 2002; Courtillot and Renne, 2003), and also from North China (Tarim; Hao *et al.*, 2003).

The sedimentary lithofacies in the Howz-e-Dorah section in Central Iran have to be considered in a context of the mid-Late Devonian volcanic activity. The temporal trend in clay mineral index (Fig. 3) is a result of climate change, and widespread volcanism would have favored the proposed greenhouse phase during the latest Frasnian (see Caldeira and Rampino, 1991; Streel *et al*., 2000; Condie *et al*., 2001; Wignall, 2001; Puffer, 2002). A change to warmer, more humid conditions during the latest Frasnian is supported by positive excursion of $^{87}Sr/^{86}Sr$ documented from the Hutk succession in south-east Iran (Mahmudy Gharaie, 2002; Matsumoto *et al*., 2002). Both volcanic activity and increased chemical weathering would develop more or less simultaneously. Enhanced weathering, induced by volcanic activity (Figs. 6 and 7B), would have facilitated the influx of Fe-enriched clays from land into the shallow marine settings of North Gondwana. The iron-rich clay minerals and other clay-size aluminosilicates were transported into the sea-water and accumulated eventually around nuclei to form oolitic ironstones.

Volcanism-induced warming during the late Frasnian may have also retarded the circulation of deep, aerated, polar waters, thus leading to a development of semi-stratified ocean conditions. The ocean turnover model by Wilde and Berry (1984, 1986) suggests that a stratified ocean basin developed and deep anoxic bottom waters were suddenly injected into normally aerated waters on the shallow marine platforms. However, the mechanism of the oceanic overturn is not fully understood. Magmatic activity may be a source of increased sea-water nutrients and may have induced ocean circulation changes leading to eutrophication and high primary productivity (Racki, 1999; Yudina *et al*., 2002), in addition to usually postulated land-derived nutrient supply (Joachimski *et al*., 2001; Chen *et al*., 2002; Godderis and Joachimski, 2004).

A warmer more humid climate during the late Frasnian, triggered by volcanic activity, is supported by geochemical and palaeobiological proxies (Frakes *et al*., 1992; Racki, 1998, 1999; Chen *et al*., 2002; Matsumoto *et al*., 2002; Mahmudy Gharaie *et al*., 2003) and by numerical modelling (Ormiston and Oglesby, 1995). However, evidence for climate cooling at the F-F boundary was also highlighted (see review in McGhee, 1996). This is largely based on study of palynomorphs (Streel *et al*., 2000), and supported by oxygen isotopic data derived from biogenic phosphates (Joachimski and Buggisch, 2002). In high-latitude regions, evidence for polar ice caps is only recorded from uppermost Famennian deposits (Sandberg *et al*., 1988; Streel *et al*., 2000). Nevertheless, a short (0.1 Ma?) glaciation may provide the



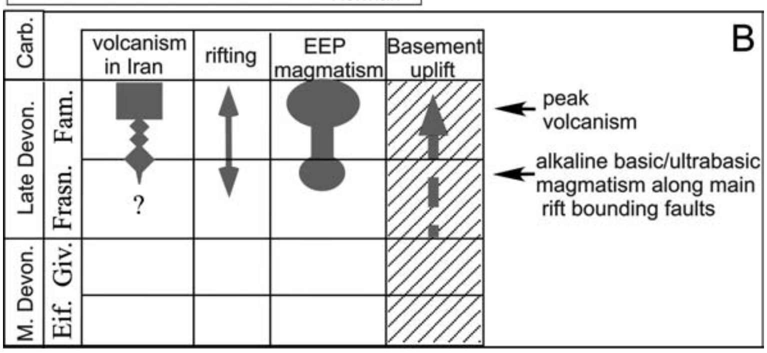


Fig. 7. A — in grey — distribution of the main areas of Late Devonian rifting and magmatism in the East European Platform (EEP; revised after Wilson and Lyashkevich, 1996, fig. 1) and the North Gondwanan domain; PDD — Pripyat-Dnepr-Donets Rift; B — timing of rifting and magmatism in Iran (based on Figure 6) and East European Platform (EEP) during Late Devonian (revised after Wilson and Lyashkevich, 1996)

most reasonable explanation for the major eustatic fall following the upper KW Event, based on the summary by Streel *et al.* (2000). On the other hand, two positive $\delta^{18}O$ excursions with high ranges of +1‰ to +1.5‰, recognized by Joachimski and Buggisch (2002), appear to correlate with positive excursions in the isotopic composition of a carbonate carbon. These isotopic data on cooling episodes seem to be in disagreement with the recent geochemical results, however, reported from South China (Chen *et al*., 2002; Mahmudy Gharaie, 2002; Ma and Bai, 2002) and Iran (Matsumoto *et al*., 2002; Dastanpour and Aftabi, 2002; Mahmudy Gharaie *et. al*., 2003) that presume a longer-term, even hyper-greenhouse effect due to hydrate dissociation. Interestingly, after examination of dispersed weathering products, Hladil (2002, p. 224) concluded that a humid warm climate dominated the F-F interval in tropical low latitudes in spite of an onset of glacioeustatic changes.

The global palaeotemperature curve by Joachimski *et al.* (2004), derived from worldwide O-isotopic values measured from conodont apatite, strongly suggests that following the greenhouse perturbation spanning the KW Crisis, climatic conditions stabilized to a very warm climate (30–33°C) that prevailed through early Famennian (since the *crepida* Chron). This contradicts the palaeobotanical evidence of Streel *et al.* (2000) suggesting a cold, dry climate, but is consistent with the increase chemical weathering rate, and evidence for volcanic activity presented in this study.

CONCLUSIONS

Sedimentological, mineralogical and geochemical evidence presented in this paper supports significant climatic changes associated with the F-F boundary interval in Iran. Increased kaolinite/illite ratios started from the late Frasnian and lasted into the Famennian. The mineralogical proxy suggests that increased chemical weathering was facilitated by warm, humid climatic conditions. Such climatic conditions promoted the release of iron-rich clay minerals finally concentrated in a cortex of ferruginous ooids. Widespread black shale deposition in the F-F boundary interval may be related to a high primary organic productivity after overall nutrient level increase in marine realms, caused by enhanced land-derived supply and/or volcanic activity.

The coincident stratigraphic position of marker clay-rich unit and ferruginous-oolite facies and basalt lava flows in Iran suggests that the climatic warming may have been caused by volcanic emission of greenhouse gases. Geological evidence presented in this study indicates that palaeoenvironmental conditions in the F-F boundary interval in Iran were considerably influenced by a change to a warmer and more humid climate.

Late Devonian rift-related magmatism in the eastern Laurussia, and northern Gondwana, would have had a significant influence on the global climate condition (Wilson and Lyashkevich, 1996), and therefore should be regarded as an important factor of the F-F environmental change. Although the main stages of at least two-step volcanism ranged probably from late Frasnian to late Famennian (like in the East European igneous domain; Fig. 7B), more refined study of temporal-spatial and geodynamic relationships of the tectono-magmatic reactivation events is required to substantiate the validity of proposed correlations and feedbacks.

Acknowledgements. We are indebted to the Director of Geological Survey of Iran (GSI) Mr. M. T. Koreiie, as well as M. Ghorashi and A. Saeidi (both GSI Tehran) for the logistic and field works supports of this study. Founding was provided by the Ministry of Education, Culture and Science of Japan. A. Navab Motlagh (GSI Tehran), J. Taheri (GSI Mashhad) and S. Monibi (Oil Company, Tehran) assisted during field works. Miss J. Komatsubara and Mrs R. Matsuda (both University of Tokyo) assisted in laboratory works. Y. Li (University of Tokyo) edited first draft of the manuscript. We are grateful to their advices, organizations and assistance in making this study possible. We wish to thank P. Wignall (University of Leeds, United Kingdom) and J. Wendt (University of Tübingen, Germany) for their insightful review and constructive comments on the manuscript. Finally, we would especially like to thank Professor G. Racki (Silesian University, Poland) for his careful and patient editing of the manuscripts, which greatly helped in improving its clarity.

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