9. Extinction models and the global extent of anoxia

9.1. Introduction

Raup and Sepkoski (1982) and Sepkoski (1996) recognised the Frasnian-Famennian event as one of the "big 5" Phanerozoic extinctions. The faunal data presented in this study confirms that a mass extinction occurred during the latest part of the *linguiformis* Zone, culminating with heavy losses at the F-F boundary. However, the cause of the extinction remains disputed - numerous causal mechanisms have been proposed since McLaren's (1970) suggestion that bolide impact was responsible. The F-F event has become widely known as the "Kellwasser Crisis" because extinction is associated with two anoxic, bituminous limestones, the "Kellwasser Horizons", in German boundary sections (Schindler, 1993), and consequently marine anoxia figures in several scenarios. The various models are summarised below, and compared with the data from this study, before a favoured extinction model is presented.

9.2. Extinction scenarios

Several extinction models have been proposed since 1970, and the majority of these fit broadly into two categories, essentially an extraterrestrial versus an earth-bound cause.

9.2.1. Bolide impact

The suggestion that the Frasnian-Famennian extinction event was the result of catastrophic bolide impact was first mooted by McLaren (1970). He proposed that a large meteorite landed in the ocean (hence the apparent absence of an impact crater), generating a giant tsunami which flooded vast areas of land. The resultant run-off from land caused the oceans to be turbid to the point of causing mass extinction. McLaren's (1970) hypothesis predates the discovery of Ir anomalies (Alvarez *et al.*, 1980) and shocked minerals (Bohor *et al.*, 1984) associated with the end-Cretaceous impact-related extinction scenario, and the only supporting evidence for McLaren's (1970) proposal was the apparently abrupt nature of the extinction. However, over the past two decades, several authors have searched for direct evidence of impact at the F-F boundary, in support of McLaren's (1970) original hypothesis (e.g. Playford *et al.*, 1984; Geldsetzer *et al.*, 1987; Wang and Bai, 1988; Goodfellow *et al.*, 1989; Wang *et al.*, 1991; Wang, 1992; Claeys *et al.*, 1994).

9.2.1.1. Iridium anomalies

Since the discovery of an Ir anomaly associated with the meteorite impact at the K-T boundary (Alvarez, *et al.*, 1980), there has been a worldwide search for a similar anomaly at the F-F boundary, but as yet definitive evidence for an anomaly at this level has not been found. Playford *et al.* (1984) identified a Late Devonian Ir peak of 0.3 ppb, 20 times above background levels, in the Canning Basin of Australia. This peak has since been dated as Early *crepida* Zone (Nicoll and Playford, 1993) and hence clearly postdates the extinction. The Ir peak occurs within a bed containing the cyanobacterium *Frutexites*, the siderophile-metabolising properties of which may have mediated the Ir enrichment (Hallam and Wignall, 1997). Elsewhere in the Canning Basin, multiple *Frutexites* beds, enriched in Ir, are separated by up to 60 cm (Goodfellow *et al.*, 1989), which also suggests that the Ir peak may not be impact related.

Wang and Bai (1988) reported two geochemically anomalous beds from South China. These are termed the "Lower *crepida* anomaly" and "Upper *crepida* anomaly" (p. 75) and are enriched in Ir by factors of 12 and 4 times background levels respectively. From their names it is clear that, as in Australia, both anomalies considerably postdate the extinction. Girard *et al.* (1997) sampled the F-F boundary interval at La Serre in detail, and found no Ir enrichment in any beds.

The only reported Ir anomaly at the F-F boundary was found by Wang *et al.* (1991) in a thin black shale in southern China, which contained 35 ppb Ir. This anomaly is rather dubious – the same bed also apparently records a sharp negative δ^{13}C shift of 7.0 ‰ (Yan *et al.*, 1993), which is at odds with carbon isotope trend in other sections (Joachimski and Buggisch, 1993). Even the various authors of Wang *et al.* (1991) could not agree on the source of the Ir anomaly: Orth and Attrep suggested a "causal relationship between Ir enrichment and a reducing environment" (p.779), while the remaining authors supported an extraterrestrial origin.

9.2.1.2. Microtektites, shocked quartz, and impact craters

Apart from Ir anomalies, there are several other lines of impact evidence, such as microtektites, shocked quartz minerals, and, of course, craters. Microtektites are tiny, glassy particles, which are produced during impact. Spherules resembling microtektites have been found in Belgium (Claeys *et al.* 1992) and in China (Wang, 1992), although both are Famennian in age and thus postdate the extinction. The Chinese examples occur in the *crepida* Zone and may be concurrent with the Canning Basin Ir anomaly. Claeys *et al*. (1994) reported glass spherules from near the F-F boundary at Hony, Belgium, which they compared to microtektites of probable impact origin, but again these were found just above the boundary.

Shock-metamorphosed quartz has not been found at the F-F boundary. The most compelling evidence for impact during the Frasnian is the Alamo Breccia, a thick deposit of limestone blocks in Nevada, which is considered to be rubble derived from bolide impact (Sandberg *et al.*, 1997), and both shocked quartz and a modest Ir anomaly are associated with this impact, although a crater has never been found. However, this impact occurred during the *puctata* Zone, some 3 my. before the F-F boundary extinction (Sandberg *et al*., 1997). Two impact craters close to the F-F boundary are known: Taihu Lake in China (Wang, 1992) and the Siljan Ring in Sweden (Claeys *et al*., 1994). The Chinese example dates from the *crepida* Zone, and may well be the source of the microspherules of the same age in China (Wang, 1992) and of the *Frutexites* bed Ir anomaly in Australia. The Siljan Ring structure dates from the *triangularis* Zone and has been proposed as the source of the microtektite-like spherules found in Belgium (Claeys *et al*., 1994). Despite the search for evidence of a latest Frasnian impact, none has been forthcoming.

9.2.1.3. Modifications of the impact scenario

Despite the lack of compelling evidence for impact during the late Frasnian, numerous authors have adhered to McLaren's (1970) original hypothesis, albeit with modifications to the scenario (Geldsetzer *et al.*, 1987; Goodfellow *et al*., 1989; Sandberg *et al.*, 1988, 2002; McGhee, 1996). Goodfellow *et al.* (1989) suggested that the global extent, magnitude, synchroneity and abruptness of the F-F event are all consistent with bolide impact as the ultimate cause. However, they stated that "it is almost imperative that such an impact is associated with one or several other processes such as sudden cooling, volcanism, hydrothermal activity, release of sedimentary prisms along continental shelves, regional chaotic debris beds due to tsunamis, poisoning of oceans and epicontinental seas with acidic and / or anoxic waters and, probably, mass killing of photosynthesizing organisms" (Goodfellow *et al.*, 1989, p. 18). Both Geldsetzer *et al.* (1987) and Goodfellow *et al*. (1989) considered the most likely cause of the F-F extinction to be the sudden overturn of anoxic waters and the poisoning of the upper water column. This is supported by the widespread distribution of anoxic facies at this time (see below) and very heavy $\delta^{34}S$ values in pyrite across the boundary, which Geldsetzer *et al.* (1987) interpret as the result of isolation of basinal waters.

Sandberg *et al.* (1988, 2002) envisaged a scenario whereby the earth was subjected to a number of oceanic impacts produced during a series of comet showers. These were considered to have caused "two short, catastrophic (sea level) rises", which "immediately preceeded the mass extinction (and) were particularly devastating to marine communities" (Sandberg *et al.,* 2002, p. 481). However, in figure 5 of their paper, Sandberg *et al.* (2002) depict the extinction level during a time of sea-level fall, so it remains unclear how they link sea-level change with bolide impacts, but earlier sea-level rises may have weakened the ecosystem, leaving it susceptible to the terminal Frasnian sea-level fall. In fact, several of the North American sections which formed the basis of Sandberg *et al.*'s (1988, 2002) hypothesis have been logged in this study, and there is little evidence for either catastrophic sea-level change, or bolide impact, during the boundary interval.

McGhee (1996) suggested that a large impact could produce global cooling of sufficient magnitude to cause the F-F extinction. Stretching the realms of the impact hypothesis to its widest boundaries, and in the absence of direct evidence for a meteorite impact near the F-F boundary, McGhee (2001) applied the "lag-time multiple impact hypothesis" (cf. Poag *et al.*, 2001) to the F-F event. He suggested that impacts several million years before the F-F boundary interrupted a global cooling trend with an anomalous warm period, and subsequently the resumption of cooling in the latest Frasnian triggered the F-F extinction.

9.2.2. Marine anoxia

Anoxic facies are widespread during the latest Frasnian, and consequently anoxia features in many extinction models. Buggisch (1972) and House (1985) were among the early proponents of the anoxia kill mechanism, suggesting that the spread of stagnant, anoxic, shallow seas during the Frasnian caused extinction amongst benthic organisms. The Late Devonian was clearly a time of widespread anoxic bottom waters, but in order to account for the widespread extinctions amongst benthos, anoxia must have spread over previously oxygenated areas. Wilde and Berry (1986) suggested this would have occurred during marine transgression, which would flood previously oxygenated areas with anoxic bottom waters. Transgression is often associated with warming, which would have the additional effect of raising the level of the oxygen minimum zone, due to the lower solubility of oxygen in warm waters. However, to cause the extinctions of reef taxa, anoxia must have spread into shallow waters. Because of the aerating effects of wind and shallow currents, surface waters should remain oxygenated, but Wilde and Berry (1986) proposed that the density stratification of the Frasnian ocean broke down as a result of cooling, causing anoxic bottom waters to rise to the surface during oceanic overturn. Geldsetzer *et al.* (1987) modified kill mechanism, substituting meteorite impact as the cause of oceanic overturn. Narkiewicz and Hoffman (1989) envisaged a similar scenario but incorporated sea-level changes, based on data from Poland. They suggested that anoxic waters formed in basinal areas, before a regressive interval caused extinction of reef organisms which were unable to migrate downslope. A subsequent transgression resulted in “a strong expansion of the oxygen minimum water layer over shelf areas, discernible in the form of *Kellwasserkalk* horizons” (Narkiewicz and Hoffman, 1989, p. 24).

Since these early, simple models, several more complex models have been proposed which involve anoxia as the proximal killer, but vary in their detail (e.g. Buggisch, 1991; Becker and House, 1994; Algeo *et al.*, 1995; Murphy *et al.*, 2000).

9.2.2.1. The Buggisch model

Buggisch (1991) proposed that a transgressive-regressive pulse, an anoxic event and a probable change in climate all occurred near the F-F boundary, and these are closely linked in his “autocyclic” extinction model (Fig. 9-1). Firstly, transgression resulted in the expansion of shelf areas, a decrease in erosion and sediment input, a decreased albedo, and consequent warming of the oceans. High organic productivity in the newly formed shallow shelf areas, combined with poor ventilation of deep waters combined to cause the extension of the oxygen minimum zone, anoxia in large ocean basins, and ultimately, mass extinction. The burial of organic carbon beneath anoxic waters led to drawdown of atmospheric carbon dioxide and global cooling, and is reflected by a positive $\delta^{13}C$ excursion in the carbon isotope record. Buggisch (1991) suggests that the icehouse effect was strong enough to form polar ice caps, leading to regression, exposure and oxidation of sediments rich in organic carbon which had been deposited on the continental shelves (reflected by a negative $\delta^{13}C$ excursion), and a gradual increase in atmospheric CO_2.

Buggisch’s (1991) model is therefore cyclic, and he imagined the Late Devonian climate alternating repeatedly between icehouse and greenhouse conditions (Fig. 9-1). The problem with Buggisch’s (1991) model is the lack of evidence for the necessary Frasnian glaciations, while the most severe glaciations should have bracketed the Upper Kellwasser Horizon. Glaciation during the Late Devonian is known only from the early Famennian of South America (Caputo, 1985). However, Buggisch (1991) argues that the South American glacial deposits have poor biostratigraphic control, and in any case, the absence of glacial deposits does not preclude Frasnian glaciation. Further, it is not clear how a decrease in erosion and sediment input, and therefore nutrient flux, could be linked to an increase in primary productivity. Nevertheless, several features of the F-F extinction fit the model well: transgression, deposition of organic carbon, a positive $\delta^{13}C$ excursion, and finally a negative $\delta^{13}C$ excursion (Buggisch, 1991).

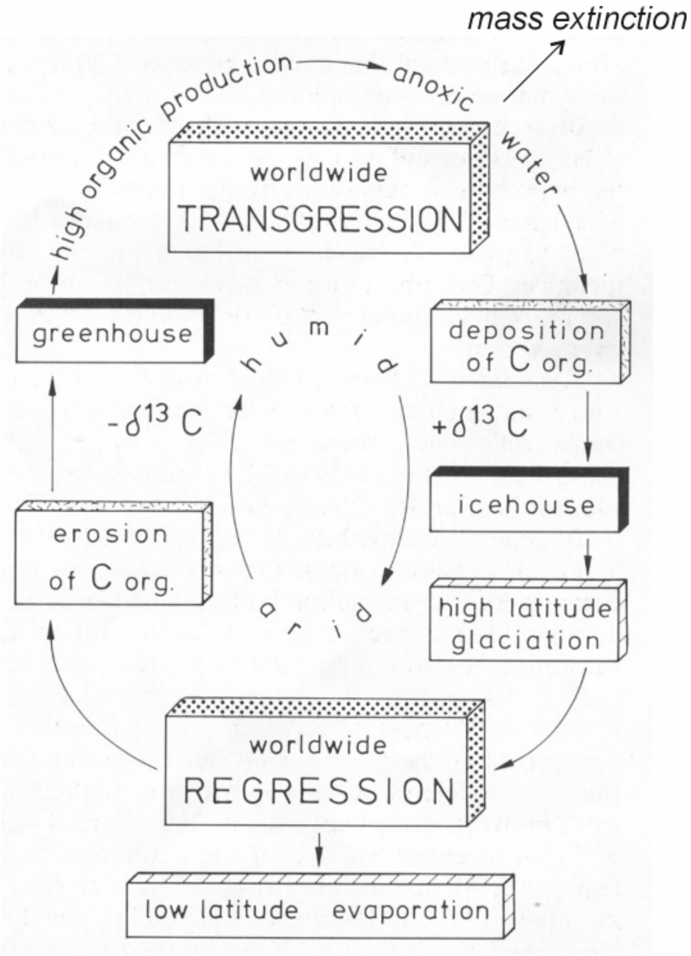

Figure 9-1: Buggisch's (1991) cyclic model for the Frasnian-Famennian mass extinction.

9.2.2.2. The Joachimski and Buggisch model

Updating Buggisch's (1991) original model, Joachimski and Buggisch (1993) incorporated warm saline waters, which would have formed on the flooded epicontinental shelves during times of transgression and sea-level highstand. These waters would then have sunk to intermediate or abyssal depths, and the resultant stratification generated anoxia, resulting in mass extinction, when primary organic carbon production was high enough to consume all available oxygen.

9.2.2.3. The Becker and House model

The model proposed by Becker and House (1994) is similar to that of Buggisch (1991) and Joachimski and Buggisch (1993) in that it incorporates several features relating to sea-level and climate change. In the absence of definitive evidence for Frasnian glaciation, Becker and House (1994) introduced oceanic volcanism (perhaps in the Panthalassa Ocean) as the ultimate cause of the mass extinction. They proposed that oceanic volcanism led to both eustatic sea-level rise and elevated atmospheric CO_2 levels, which promoted the formation of large volumes of warm saline bottom waters.

Although warm, these waters were dense, and caused the displacement and upwelling of cool, deep waters, which were particularly nutrient-rich. Becker and House (1994) proposed that this upwelling caused a drastic increase in primary productivity, faunal blooms in the Kellwasser beds, and increased burial of organic matter in black shales and limestones. High productivity and the associated biogenic oxygen consumption generated benthic anoxia, causing mass extinction amongst benthic organisms in areas where the Kellwasser facies developed. This does not account for extinctions amongst pelagic groups, or in shallow waters, and Becker and House (1994) therefore further proposed that climatic overheating induced lethally high water temperatures, which were responsible for the demise of corals, stromatoporoids and other shallow-water organisms. Subsequently, regression is thought to have been responsible for further destruction of shallow water habitats, and a reduction in “ecospace” for pelagic groups (Becker and House, 1994, p. 68). The burial of large amounts of organic carbon led to a decrease in atmospheric CO_2, diminishing the greenhouse effect, and bringing the upwelling cycle, and the mass extinction, to an abrupt end in most areas at the terminal Frasnian.

9.2.2.4. The Algeo model

A model linking changes in both the marine and terrestrial biospheres, and in particular giving attention to the role of plants, was first proposed by Algeo *et al.* (1995) and has been subsequently revised by Algeo and Scheckler (1998). While Algeo and Scheckler (1998) stress that terrestrial-marine teleconnections are poorly understood, it is known that the mass extinction coincides with important developments in plants, and their extinction model considers these developments to be the “root” cause. They suggest that two major innovations amongst plants, arborescence (tree stature, with necessarily deeper roots), and the development of seeds, promoted a large increase in soil formation. This is postulated to have enhanced chemical weathering, increased riverine nutrient fluxes to the ocean, caused eutrophication, high primary productivity, and thus, as in the Becker and House (1994) model, widespread bottom water anoxia, resulting in mass extinction. In turn the burial of large amounts of organic carbon is suggested to have drawn down atmospheric CO_2, causing global cooling and eventually a brief glaciation during the Famennian (Algeo and Scheckler, 1998). The model therefore incorporates both anoxia and cooling, although only anoxia is suggested to be the cause of the mass extinction.

The Algeo model neatly ties together the undoubted changes in the terrestrial biosphere with the well-documented changes in the ocean. However, the problem remains of the exact timing of the important evolutionary steps amongst plants, and therefore the degree to which chemical weathering increased during the Frasnian (Hallam and Wignall, 1997). The largest trees, the archaeopterids, were mostly limited to floodplain habitats (Beck, 1964; Thomas and Spicer, 1987) and the earliest known seeds are mid to late Famennian in age (Algeo and Scheckler, 1998), thus upland areas were probably not colonised during the Frasnian. Increased chemical weathering may not have become a significant factor until well after the F-F extinction.

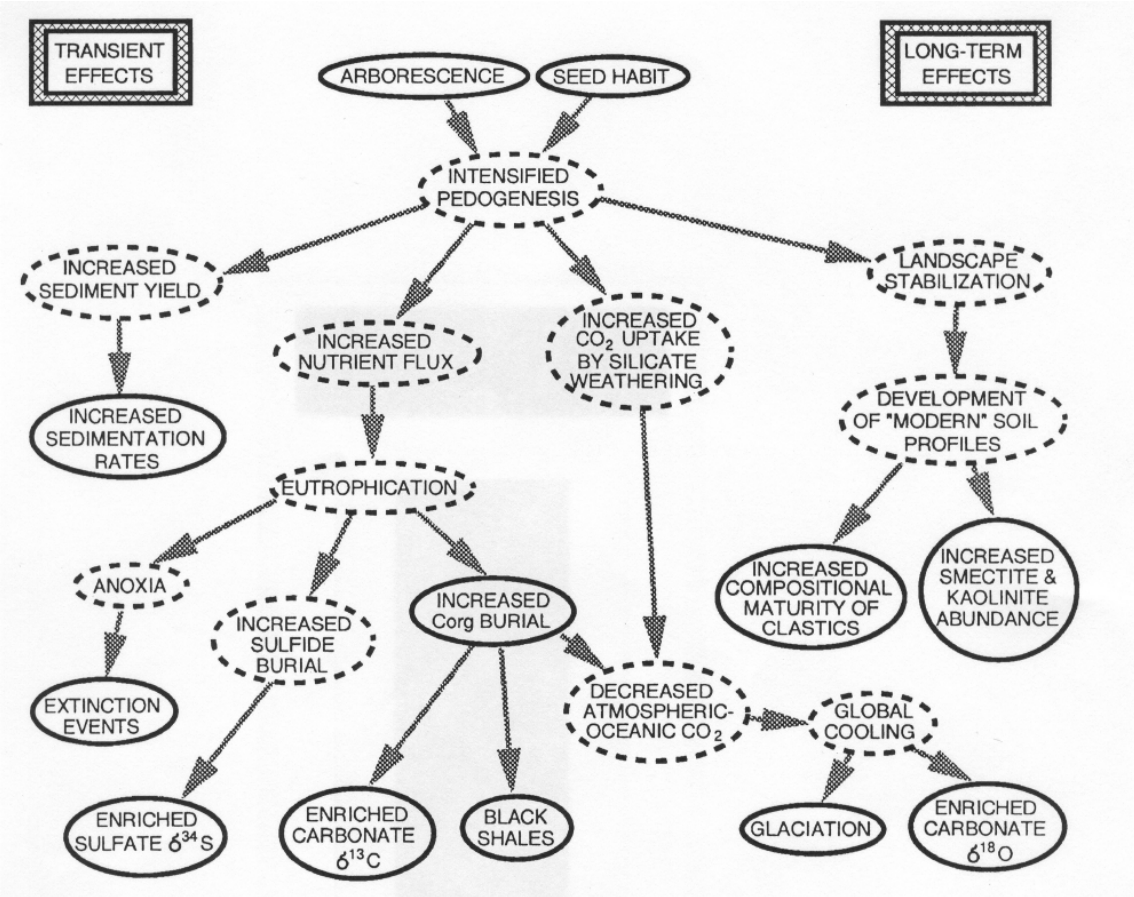

Figure 9-2: Flow chart model of Algeo and Scheckler (1998) linking the development of arborescence and seeds amongst plants to oceanic anoxia and mass extinction. Solid outlines indicate documented geological records.

9.2.3. Marine regression

It has long been argued that sea-level change and mass extinction events are causally linked (Hallam, 1981; Flessa *et al.*, 1986; Hallam and Wignall, 1999). Johnson (1974) was the first to imply sea-level fall in the Frasnian-Famennian extinction scenario. The Devonian was a time of sea-level highstand (e.g. Johnson *et al.*, 1985; McGhee, 1996), but the overall rising sea-level trend of the Frasnian is punctuated by several short-term regressions (e.g. cycle IIc of the Johnson *et. al.* (1985) sea-level curve, see figure 9-3). Johnson (1974) suggested that a rapid regressive-transgressive pulse occurred during the late Frasnian, which eliminated "perched" faunas, which had colonised widespread shelf areas during this period of high sea-level.

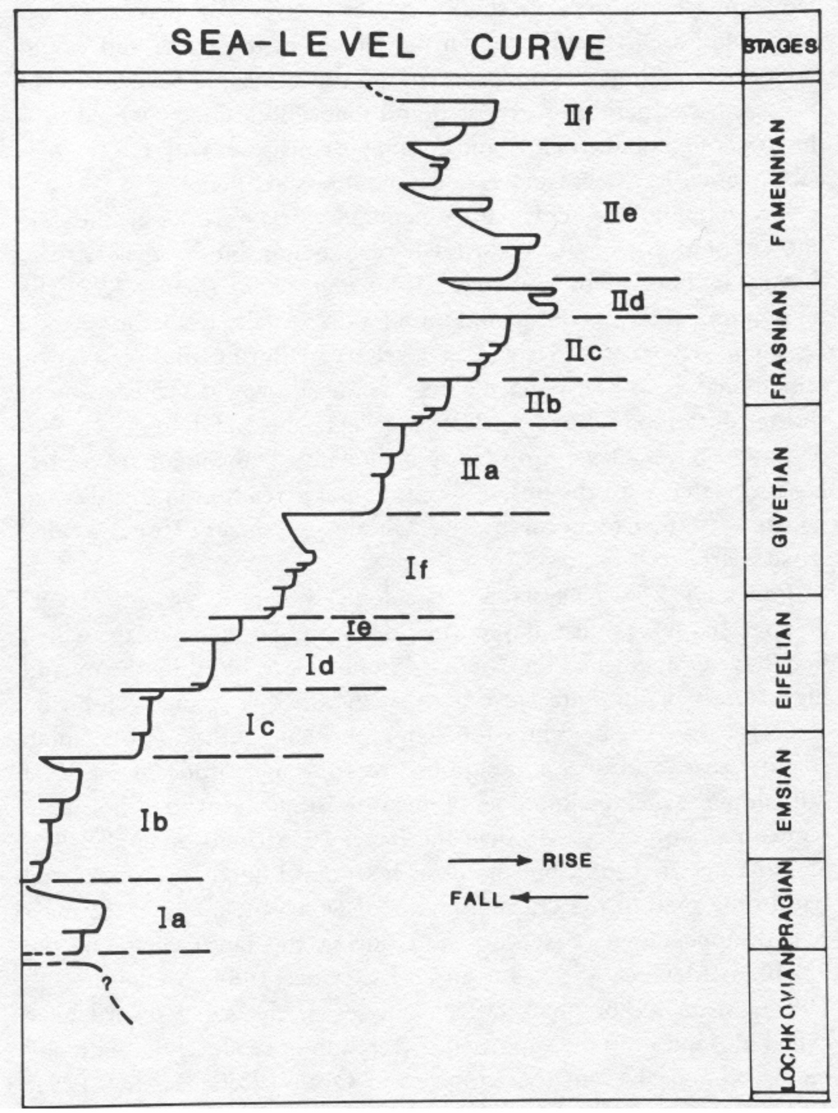

Figure 9-3: Sea-level curve of Johnson *et al.* (1985). Note that the latest Frasnian records a period of transgression before a sharp regression in the basal Famennian.

Several arguments against the regression-induced extinction hypothesis may be raised. Firstly, it does not explain widespread extinctions amongst pelagic groups, nor does it account for the fact that shallow water benthos would simply move downslope during a regressive event. Secondly, it is not clear why only regression in the late Frasnian should cause mass extinction, when there are numerous other regressive episodes later in the Famennian. A sea-level fall near the F-F boundary was also proposed by Sandberg *et al.* (1988), Morrow (2000), and Sandberg *et al.* (2002), based upon conodont biofacies, specifically the "bloom" of the presumed shallow-water icriodids, although as has already been discussed, this has an alternative explanation. In fact, contrary to the aforementioned authors, a late Frasnian regression is not supported by sedimentological data from this study. Subsequently, the classic Johnson *et al.* (1985) sea-level curve has been reproduced and / or modified, with considerable inconsistencies (most recently by Devleeschouwer *et al.* (2002), and Chen and Tucker (2003)). In most cases, this has the effect of shifting the sea-level curve upwards, with the result that the F-F boundary actually falls within a transgressive episode!

9.2.4. Rapid climate change

Although climate change is implicit in most, if not all, extinction models, the model of Fischer and Arthur (1977) holds tectonically induced climate change as the sole cause. They devised a climate model based upon changes in the configuration of the earth's mantle and core, and divided the Phanerozoic into five "icehouse" and "greenhouse" periods.

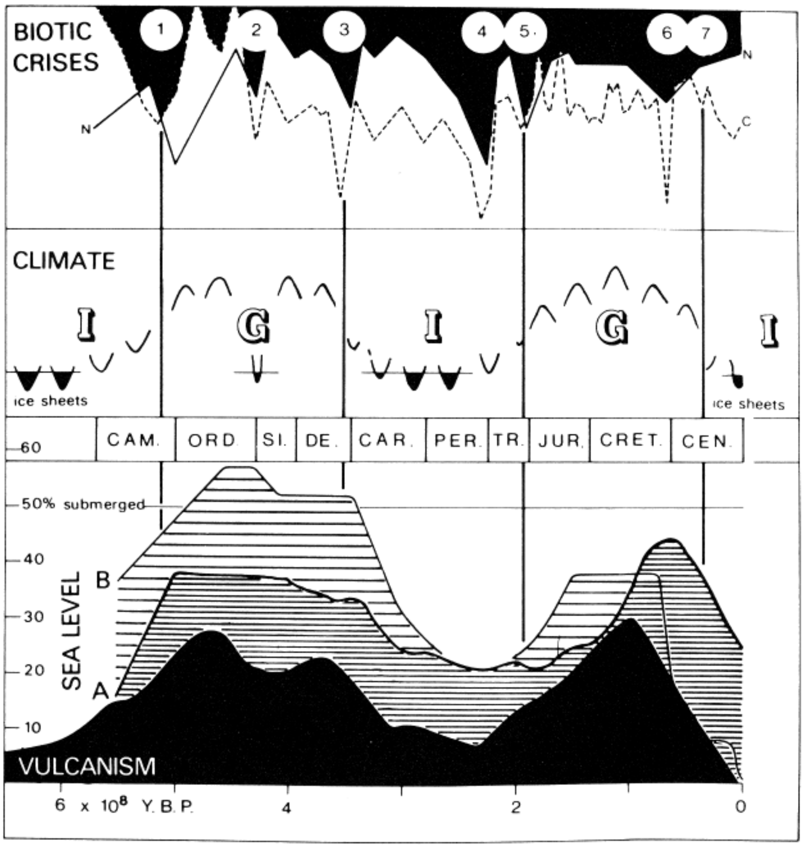

Figure 9-4: Global climate for the Phanerozoic, proposed by Fischer and Arthur (1977). Climate varies between icehouse ("I") and greenhouse ("G") periods, and is correlated with sea-level changes (lines A and B), volcanism, and mass extinction events (top of figure). From Fischer (1984).

Fischer and Arthur (1977) suggested that rapid climate change, rather than extremes of hot or cold conditions, was behind mass extinction, and predicted that when temperature change was at its most rapid, extinctions would occur. They demonstrated that the Late Devonian, end-Permian, end-Triassic, and end-Cretaceous extinctions all occurred during such times (Fig. 9-4), with the Frasnian-Famennian interval being a time of rapid cooling. However, the temporal resolution of Fischer and Arthur’s (1977) climate change curve is low – according to figure 9-4, climate was cooling throughout the Late Devonian and into the Carboniferous. Glacial deposits are known from the middle Famennian of South America (Caputo, 1985), which suggests that the climate was already cold by this time, but it is almost impossible to suggest that the rate of climate change was at its highest in the late Frasnian.

9.2.5. Global cooling

Cooling is one of the more plausible causes of the extinction and has been implicated by Copper (1977, 1986), McGhee (1989, 1996) and Joachimski and Buggisch (2002), although a problem arises in the ultimate cause of global cooling, wherein the models differ. Widespread evidence supports the death-by-cooling hypothesis (e.g. Copper, 1986; McGhee, 1996):

1) both marine and terrestrial biospheres were affected during the extinction,
2) the preferential elimination of reef taxa and other low-latitude faunas,
3) latitudinal compression of geographic range in surviving low-latitude faunas,
4) the proliferation of cold-water groups (such as hexactinellid sponges, tornoceratid ammonites, and labechiid stromatoporoids) during and after the extinction interval,
5) the presence of glacial sediments in Brazil.

Copper (1986) proposed that important changes in global palaeogeography at the Frasnian-Famennian boundary had severe climatic implications. In his model, the continents of Euramerica / Laurussia and Gondwana were separated by an ocean during the Frasnian (the “Frasnian ocean”), which closed at the F-F boundary (Fig. 9-5). The suturing of these two continents resulted in a large continental plate, straddling the equator. This disrupted low-latitude, easterly currents, bringing high-latitude, cold waters into equatorial regions, along the western margins of the new supercontinent (Fig. 9-5). Restricted oceanic circulation is suggested to have produced euxinic conditions in basins in the palaeo-Tethys region. Like the Algeo model, Copper (1986) incorporates both global cooling and low-latitude anoxia into his extinction scenario, although unlike Algeo and Scheckler (1998), only cooling is suggested to have caused mass extinction.

Copper’s (1986) palaeogeographically forced climate cooling mechanism has since been brought into doubt, as neither palaeomagnetic data (Van der Voo, 1988) nor biogeographic data supports a collision of Euramerica and Gondwana at the Frasnian-

Famennian boundary. Scotese and McKerrow (1990) support such a collision, but suggest that it occurs in the Early Devonian. A further problem with Copper's (1986) model is that of all the extinction mechanisms, it should be one of the most gradual (because it relies on continental drift), thus Copper (1986) stresses the gradual nature of the extinctions. However, as demonstrated in chapter 8, most faunal data suggests that the extinction was limited to the latest *linguiformis* Zone, and was not Frasnian-long as Copper (1986) suggests.

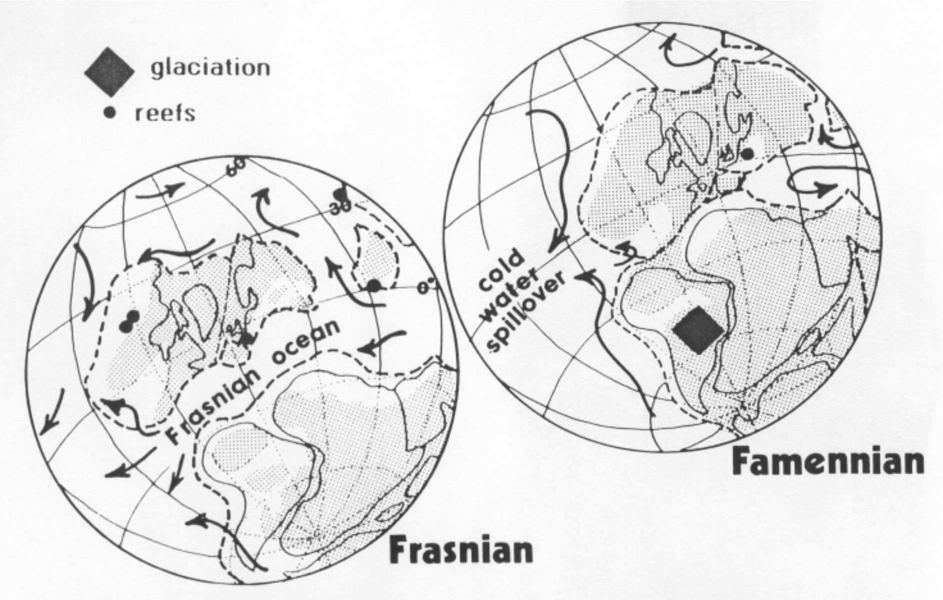

Figure 9-5: Copper's (1986) model of Frasnian-Famennian palaeogeography. Suturing of Euramerica and Gondwana at the F-F boundary is suggested to have caused high-latitude, cool water to flow into equatorial regions, causing mass extinction by cooling.

Joachimski and Buggisch (2002) measured $\delta^{18}O$ signatures for the Frasnian-Famennian interval, using conodonts. Based on this, they suggested a cooling of low-latitude surface waters of 5 - 7º C during the latest Frasnian, and proposed that repeated temperature changes were responsible for the extinction. Again, Joachimski and Buggisch (2002) consider that the preferential extinction of low-latitude organisms, and the bloom of hexactinellid sponges, both support the cooling hypothesis. The oxygen isotope data of Joachimski and Buggisch (2002) is contrary to that of Brand (1989, 1992) which indicated exceptional warming during the late Frasnian, with cooling not occurring until the mid Famennian.

Finally, McGhee (1996) favours a model whereby a bolide, or a series of closely spaced bolides, impacted and produced a huge dust cloud, which cooled the Frasnian climate. This represents a more rapid way of cooling the earth's climate than Copper's (1986) model, but as discussed earlier, the evidence for bolide impact is rather unsubstantiated.

Although substantial evidence for climate cooling has been presented by Copper (1977, 1986), McGhee (1989) and Joachimski and Buggisch (2002), much of this evidence is open to alternative interpretation. These authors considered the preferential elimination of low-latitude faunas, and the blooming of supposed cool water organisms to support the cooling hypothesis. However, there is too little data from high-latitude sections to confirm this selectivity, and Yudina *et al.* (2002) has recently shown that the extinction was probably just as severe at higher latitudes. Hallam and Wignall (1997) point out that the most successful surviving faunas have not only a cool-water preference, but also a deep-water preference, and thus their survival could equally reflect the spread of deep-water facies during the transgressive interval associated with the Upper Kellwasser Horizon. A final, unanswered question is what drove the proposed cooling? Palaeomagnetic and biogeographic evidence does not support the palaeogeographically-forced cooling model of Copper (1986). Neither is there any evidence to suggest that climate cooling was driven by glaciation – the glacial evidence from Brazil is of Famennian age (Caputo, 1985).

9.2.6. Global warming

In contrast to the evidence for cooling, Thompson and Newton (1989), Brand (1989), and Ormiston and Oglesby (1995) all support a death-by-warming hypothesis. Thompson and Newton (1989) note that many marine organisms live close to the upper limit of their temperature tolerance, and thus mass extinction could be brought about by only a small increase in temperature. Thompson and Newton (1989) suggested that the already high surface temperatures increased further during the Frasnian, causing the expansion of the oxygen minimum zone, and marine organisms were lethally trapped between anoxic water below, and water that was too warm above.

Global warming is supported by $\delta^{18}O$ isotope values, and Brand's (1989) data, based on isotopes from brachiopod shells, indicates exceptionally high water temperatures during the Devonian, reaching as high as 60° C at the F-F boundary. Clearly this is an unrealistic estimate for palaeotemperature, thus Brand (1989) adjusted the palaeotemperature, suggesting instead that temperatures only became lethally high, reaching perhaps 40° C, at the F-F boundary. In fact, the peak of warming in Brand's (1989) data actually post-dates the F-F boundary. Even an estimate of 40° C is an unreal estimate of palaeotemperature – such a temperature should still have produced 100% extinction.

Oxygen isotopes are highly susceptible to diagenetic alteration, which was almost certainly responsible for Brand's (1989) unrealistic results. Indeed, several other oxygen isotope studies have produced quite different temperature estimates: Popp *et al.* (1986) and Wadleigh and Veizier (1992) had a broad range of temperatures for the entire Devonian, and, more recently, using oxygen isotopes from conodonts, Joachimski and Buggisch (2002) implicated global cooling in the mass extinction scenario. Notwithstanding the conflicting oxygen isotope signals, ecological evidence argues against the global warming hypothesis. Warming should preferentially eliminate faunas at the highest latitudes, but it is widely noted that tropical faunas are the most severely affected (although Yudina *et al.* (2002) suggest that mid-latitude faunas were also affected). In warmer seas, reefal ecosystems would have flourished and tropical faunas would have expanded their geographical ranges into high latitudes (McGhee, 1996), whereas in reality, reef taxa are amongst the most notable casualties of the event.

9.2.7. Eutrophication

Murphy *et al.* (2000) suggested that the mass extinction was linked to episodes of eutrophication during the late Frasnian. In normal marine surface waters, photosynthesis gives rise to the Redfield C:N:P ratio of 106:16:1. N and P are the two main limiting nutrients controlling primary productivity (Broecker and Peng, 1982), and in offshore settings, it is the regeneration of N and P during organic matter decomposition that determines their availability (Tyson and Pearson, 1991). In Murphy *et al.*'s (2000) model, N and P are preferentially released into the water column from organic matter during bacterial decomposition, under variable redox conditions. This is manifest as a shift in the C:N:P burial ratio from normal values to ~5000:150:1 in the equivalents of the Kellwasser horizons in New York State. Global cooling is suggested to have increased seasonality and driven short-term stratification and mixing, which returned the excess nutrients to surface waters, enhancing primary productivity and resulting in eutrophication (Murphy *et al.*, 2000). Eutrophication is suggested to have resulted in mass extinction because firstly, high surface-water productivity resulted in a loss of water clarity, and secondly, eutrophication led to the development of benthic anoxia. The eutrophication process is suggested to have locally increased the burial of organic carbon, which is reflected in New York State as positive $\delta^{13}C$ excursions across each of the Kellwasser horizons (Murphy *et al.*, 2000). Murphy *et al.* (2000) point out that Devonian shallow-marine ecosystems may have been characterised by oligotrophic conditions (e.g. Martin, 1995), and thus the effects of eutrophication would have been particularly catastrophic for such organisms. Thus, the eutrophication mechanism provides an unusual hypothesis, which ties together the evidence for anoxia and cooling. However, since eutrophication is a local phenomenum, whether this mechanism could be responsible for globally widespread anoxia, as well as extinctions outside of shallow marine settings, is open to doubt.

9.3. Summary of evidence

9.3.1. Faunal changes

As demonstrated in chapter 8, the Frasnian-Famennian mass extinction saw relatively abrupt and widespread losses of organisms during the latest *linguiformis* Zone. Calculation of the extinction rate, based on the range charts presented in figures 8-1, 8-2, 8-3 and 8-4, shows that 71% of species, representative of a broad range of habitats, present during the *linguiformis* Zone did not cross the F-F boundary. The vast majority of these extinctions are temporally confined to the upper part of the German Upper Kellwasser Horizon, or its global equivalents. Cool and / or deep-water faunas appear to have survived the extinction best. Whether this was because they were more tolerant of (potential) global cooling during the crisis interval, or because they survived in deep waters beneath the oxygen minimum zone remains unclear.

9.3.2. Anoxia

The evidence for globally widespread anoxia and contemporaneous mass extinction presented in this study strongly suggests that the two are causally linked. The nature of the late Frasnian anoxic “Kellwasser” events can be summarised as follows:

- European submarine rise sections, located on opposite sides of the Prototethys (e.g. Steinbruch Benner, Germany, and Coumiac, France) record two discrete anoxic events, the classic Kellwasser Horizons within an otherwise well-oxygenated depositional history. These occur near the Early-Late *rhenana* Zone boundary, and in the topmost *linguiformis* Zone (Fig. 9-6), up to the F-F boundary (the Upper Kellwasser Horizon).
- In European epicontinental basin / basin-slope settings (e.g. Kowala Quarry, Poland, and La Serre, France), dysoxia or anoxia prevailed through much of the late Frasnian, intensifying to anoxic or euxinic conditions during the Lower and Upper Kellwasser events. The F-F boundary beds record the most intense period of anoxia, in the latest part of the *linguiformis* Zone (Fig. 9-6).
- There is evidence to suggest that the latest part of the *linguiformis* Zone records an incursion of anoxic waters into otherwise well-oxygenated, very shallow-water environments (e.g. Psie Gorki, Poland).
- Sections in the western United States record anoxic events from the margins of a separate ocean to those in Europe, and thus significantly broaden the global distribution of the data (Fig. 9-6). Hemipelagic sedimentation on the slopes of

both the Pilot Basin (Coyote Knolls) and the Woodruff Basin (Devil's Gate) records dysoxic or anoxic conditions throughout much of the late Frasnian. These conditions are frequently interrupted by allochthonous sediment gravity flows containing a rich shelf fauna, suggesting that conditions up-slope were oxygenated. In both basins, oxygen levels deteriorated and euxinic conditions developed during the latest *linguiformis* Zone. The sections at Northern Antelope Range and Tempiute Mountain also record anoxic conditions on the slope of the Woodruff Basin, but their record is mostly obscured by the large amount of allochthonous sediment input.

- In deep basin-floor settings in the western United States, the Whiterock Canyon section records persistent anoxia throughout the Early *rhenana* to *triangularis* Zones, but the most intensely euxinic period occurs at the base of the *linguiformis* Zone. Nevertheless, conditions at the boundary remained anoxic. The more distal Warm Springs section records dysoxic sedimentation through the same interval, but with an anoxic pulse during the latest *linguiformis* Zone, which persists into the early Famennian. In both sections, anoxia does not reach the same intensity as in slope settings, and it is likely that the basin floor lay beneath the oxygen minimum zone, which developed over the basin slopes.
- Shallow-water sections in the western United States have not been studied, due to the lack of available sections, but the paucity of allochthonous shelf fauna and the presence of flat pebble conglomerates, immediately above the F-F boundary at Coyote Knolls, suggests that anoxic conditions may have developed on the shelf at the F-F boundary.
- The Beaver Meadow Creek section in New York State provides additional evidence for anoxia from a separate foreland basin, a considerable distance from those sections in the Europe and the western United States. This section exposes sediments from a basal slope / basin floor setting in the Appalachian basin, and records an upper dysoxic depositional history throughout the Early *rhenana* to *triangularis* Zones, punctuated by numerous anoxic events. The most persistent and intensely euxinic of these occurs during the latest *linguiformis* Zone and persists into the early Famennian. A Lower Kellwasser Horizon equivalent, the Pipe Creek Shale, can also be recognised during the top part of the Early *rhenana* Zone.

Thus, equivalents of the classic Lower and Upper Kellwasser horizons of German boundary sections can be recognised in many facies around the world. The degree and duration of oxygen restriction in the Late Devonian seas was clearly related to palaeobathymetry, with deep water and / or basinal locations, such as Kowala, La

Serre, Devil's Gate and Coyote Knolls recording prolonged periods of dysoxic / anoxic deposition. However, pyrite framboid data indicate variation in the intensity of oxygen restriction. The F-F boundary in particular saw the establishment of permanent euxinicity in European and American basins, with sulfidic waters probably extending up to the photic zone in Poland (Joachimski *et al*. 2001). In European basins in particular, this development of a substantial volume of sulphidic lower water column probably ensured that high-energy events, such as storms, were not even able to transiently oxygenate the seafloor in epicontinental basins. This interval also saw the expansion of oxygen-poor waters into shallower water settings including submarine highs and probably even reef-crest locations. Other shallow-water Polish sections also reveal dysoxic deposition across the F-F transition based upon V/Cr ratio evidence (Racki *et al*., 2002).

The Upper Kellwasser anoxic event is thus seen to be intensive and extensive, and, crucially globally synchronous. The same cannot be said of the Lower Kellwasser event: in Germany, the Lower Kellwasser Horizon is within the early part of the Late *rhenana* Zone, but at Kowala Quarry in Poland, it occurs much later, near the top of the Late *rhenana* Zone. In New York State, the equivalent anoxic event occurs earlier, at the top of the Early *rhenana* Zone. Feist and Schindler (1994) have previously noted a non-synchroneity between French and German developments of Lower Kellwasser "dark facies" as have Crick *et al*. (2002), based on magnetic susceptibility correlation data. Synchroneity is the key difference between these two anoxic events – and an explanation as to why only the anoxic event during the latest *linguiformis* Zone saw catastrophic faunal losses, because only at this time did anoxic water invade several facies at the same time around the world.

9.3.3. Comparison of data with previous models

In the absence of evidence for impact during the Frasnian-Famennian extinction interval, an exclusively earth-bound scenario for the mass extinction is likely. Near-conclusive evidence suggests that anoxia had a major role in the extinction. As described earlier in this chapter, several models incorporating death by marine anoxia have been proposed by former workers. However, there may have been extinctions amongst terrestrial flora (e.g. Richardson and McGregor, 1986; McGhee, 1996), although details of these changes are unknown. Marine anoxia cannot itself account for terrestrial extinctions, and thus some other mechanism (e.g. climate change) should perhaps also figure in the model. The big question, of course, is what might have been responsible for the late Frasnian anoxic event, for this was the ultimate cause of the extinction. Several possibilities are put forward later in this chapter.

The data suggests that bottom-water anoxia first developed in epicontinental basins in the late Frasnian, before spreading into the upper water column, and into shallow-marine areas close to the F-F boundary, as a result of expansion of the OMZ. This model for the development of anoxia during the F-F interval contrasts with models proposed by several previous workers (Fig. 9-6). They postulated that anoxic waters were displaced into shelf locations from deep, oceanic settings (Goodfellow *et al*. 1989), either by sinking of dense, cold waters (Wilde & Berry, 1986), or warm, saline waters (Becker & House 1994). In Joachimski & Buggisch's (1993) variation, enhanced warm, saline bottom water generation on flooded highstand shelves is considered to have intensified the oceanic oxygen minimum zone with the result that anoxic waters spread back across the shelf. Implicit in these models is the idea that "deeper anoxic waters *must* [my italics] be brought out of the deeps and spread over previously oxygenated regions of the seafloor" McGhee (1996, p. 156). However, it is not a mandatory requirement of anoxic events that they can only begin in oceans as the Upper Kellwasser Event demonstrates. The preferential survival of the deepest water fauna, such as solitary Rugosa (Sorauf & Pedder 1986) and the Thuringian ostracod community (Lethiers & Casier 1999), together with pyrite framboid data from the deepest water sites, during the Kellwasser crisis suggests that bathyal and deeper waters were not the site of the most intense anoxia (Fig. 9-6) and probably lay below the oxygen minimum zone. However, deepest water trilobite taxa appear to have faired rather badly compared to their shallowest water cousins (Feist & Schindler, 1994). A further, potential counter-argument may be had from contemporaneous changes in pyrite S isotopes that can be interpreted as evidence for stratified, euxinic oceans in the Frasnian (Goodfellow *et al*. 1989). Goodfellow *et al*. 1989 suggested that anoxic waters formed in stratified oceanic basins by prolonged activity of sulphate-reducing bacteria, which selectively reduced ^{32}S, resulting in a shift to more positive δ^{34}S values in dissolved sulphides. Oceanic overturn transported this anoxic water into shelf areas, where pyrite enriched in ^{34}S was precipitated. Thus the off-reef succession at Medicine Lake, Alberta, records highly positive δ^{34}S values (Goodfellow *et al*. 1989). Such isotopic studies are rare, and clearly an area for future research.

Aside from discrepancies regarding the site of formation of anoxic waters, the data from this study best fits the models of Wilde and Berry (1986), Joachimski and Buggisch (1993) and Becker and House (1994). Wilde and Berry (1986) suggested that basinal anoxia spread over previously oxygenated areas during marine transgression. Transgression is often associated with warming, which would have the additional effect of raising the level of the oxygen minimum zone, due to the lower solubility of oxygen in warm waters. Subsequent cooling (in the latest Frasnian) is suggested to have caused the density stratification of the Frasnian ocean to break down, causing anoxic bottom waters to rise to the surface during oceanic overturn at the F-F boundary. There is evidence also for high-energy events at the F-F boundary, which could also have caused the destabilisation of the water column. The relatively rapid expansion of anoxic bottom-waters during overturn might account for the abrupt nature of the mass extinction of benthic and pelagic faunas, although the effects of overturn would be brief, due to rapid reoxidation of dissolved sulphides. This is seen in the modern-day Black Sea, where mixing of anoxic deep waters results in only transient presence of H_2S in surface waters (Beznosov, 2000). Sedimentological evidence to support deepening is observed during the Early *rhenana* Zone in the western United States. Support for cooling is less forthcoming, but there is evidence of regression in several sections in the early Famennian, which may be the long-term result of cooling that began in the Frasnian, and may have ultimately led to Famennian glaciation. In addition, the flourishing of presumably cold-water groups during and after the extinction event has been taken as evidence for cooling (e.g. Copper, 1986).

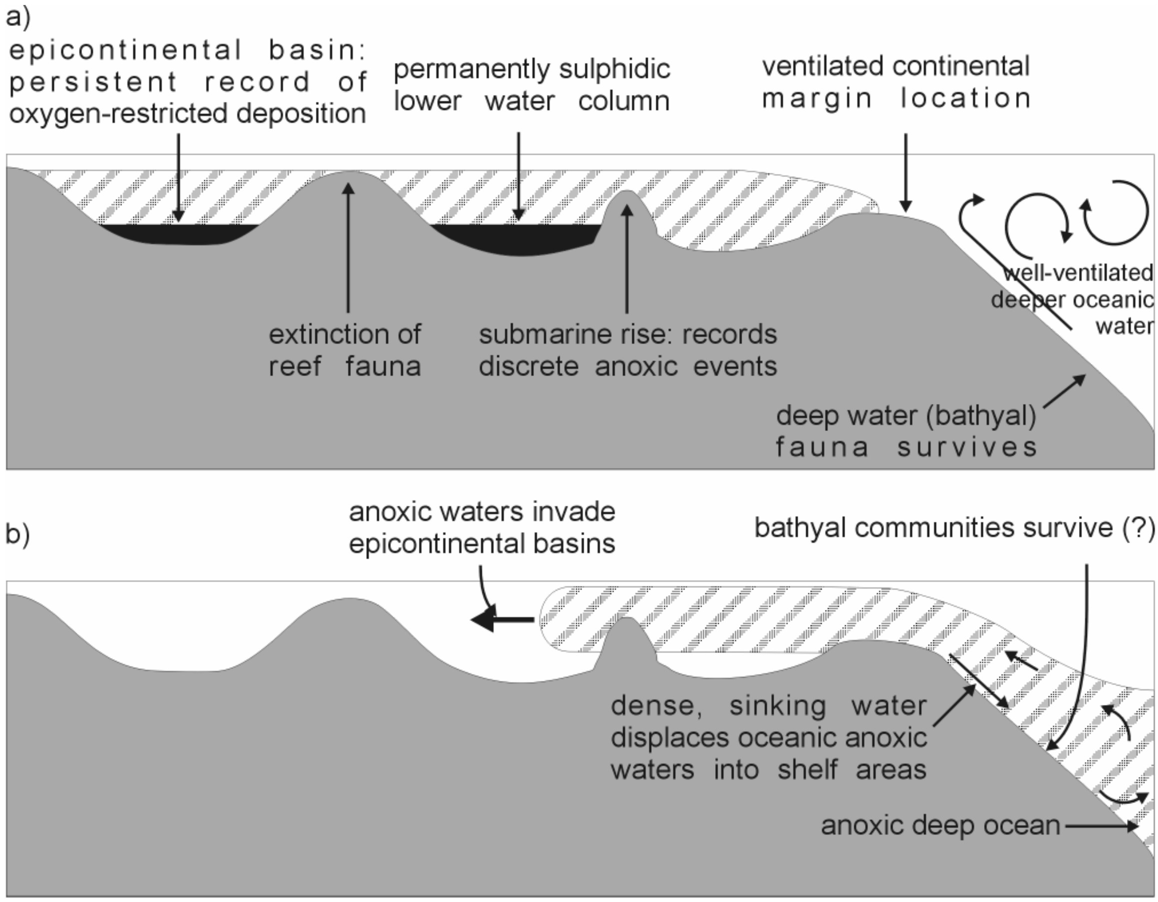

Figure 9-6: Comparison of model proposed here (a) for the development of anoxia during the Kellwasser anoxic events with previous suggestions (b) that the shelf anoxia was a consequence of oceanic upwelling of deep anoxic waters. Evidence for a well-ventilated continental margin environment is provided by the Wolayer Glacier section in Austria (see Bond *et al.*, 2004).

In the absence of evidence for Frasnian glaciation, Becker and House (1994) modified the model of Joachimski and Buggisch (1993), introducing oceanic volcanism as the ultimate cause of the mass extinction. This is suggested to have resulted in both eustatic sea-level rise and elevated atmospheric CO_2 levels, which promoted the formation of dense, warm saline bottom waters. Oceanic warming may have been a by-product of volcanism, but as noted, the evidence for warming or cooling is not clear. Becker and House (1994) argued that marine anoxia at the F-F boundary was not global in extent, and introduced warming into the scenario to account for extinctions in locations where the Kellwasser facies are not developed, such as the Canning Basin, Australia. However, it has been shown that anoxic waters may have spread into such environments without resulting in black shale or limestone deposition (e.g. at Psie Gorki, and in the western United States), and probably had far greater extent than Becker and House (1994) realised, thus anoxia alone can account for worldwide marine extinctions.

Both the models of Wilde and Berry (1986) and Becker and House (1994) are good candidates for the extinction mechanism. At present, there is no real control on variations in temperature during the crisis interval, and thus neither model can be proven correct or otherwise, although some form of climate change might account for terrestrial extinctions. However, transgressive events and widespread black shale deposition is usually associated with warming, rather than cooling, because of the lower solubility of oxygen in warmer water. Joachimski *et al.* (2001) suggested that sulfidic waters probably extended up to the photic zone in Poland, a scenario that would surely require high surface water temperatures. The most widespread phase of oceanic anoxia of the Cretaceous occurred during a period of volcanically driven global warming in the late Cenomanian (Keith, 1982; Kerr, 1998). In many respects, the Cenomanian-Turonian extinction is similar to the F-F event, although the former was an oceanic anoxic event (OAE) (Schlanger and Jenkyns, 1976), whereas the latter appears to have been mostly restricted to epicontinental and shelf settings. Nevertheless, several aspects of Kerr’s (1998) C-T extinction model may apply here. Kerr (1998) suggested that submarine volcanism caused both direct hydrothermal warming of the oceans and indirect warming through release of CO_2 to the atmosphere. Acidification of the ocean due to volcanic SO_2 emissions caused further release of CO_2 and led to a runaway greenhouse. This warming trend ended abruptly in the Turonian, perhaps through a negative feedback loop (as in the Algeo *et al.* (1995) model for the F-F extinction), which saw high primary productivity, and the burial of large amounts of organic CO_2 in black shales. Schlanger and Jenkyns (1976) suggested that the extensive black shale deposition during the late Cenomanian was the result of the expansion of the oxygen minimum zone during periods of enhanced primary productivity, a mechanism which also features prominently in Becker and House's (1994) model for the F-F event.

9.4. A new model for the Frasnian-Famennian extinction

The models of Wilde and Berry (1986), Joachimski and Buggisch (1993), and Becker and House (1994) have here been modified, and the following scenario for the F-F mass extinction is proposed:

- the late Frasnian was a time of warm climate and sea-level highstand. A transgression occurred during the Early *rhenana* Zone.
- anoxic bottom waters formed in large areas of geographically widespread epicontinental basins during the late Frasnian, with oxygen minimum zones forming on basin slopes.
- anoxia intensified during the latest *linguiformis* Zone, and expansion of the oxygen minimum zone saw an incursion of anoxic waters into previously oxygenated shelf environments, and into the upper water column, resulting in deposition of the classic "Upper Kellwasser Horizon" in submarine rise settings. Just beneath the F-F boundary, anoxia reached very shallow-water habitats.
- a possible explanation for the expansion of the oxygen minimum zone may have been increased productivity in surface waters, which led to biogenic consumption of dissolved oxygen at depth, and burial of large amounts of organic carbon.
- simultaneous, globally widespread anoxia, in a variety of environments, resulted in catastrophic ecospace reduction and the poisoning of both benthic and pelagic groups. This is recorded by a rapid mass extinction within the latest *linguiformis* Zone Upper Kellwasser Horizon, culminating at the F-F boundary.
- the crisis comes to an abrupt end at the F-F boundary. The burial of a large amount of organic carbon in the latest Frasnian led to the drawdown of atmospheric CO_2, resulting in global cooling and an improvement in environmental conditions. The basal Famennian ostensibly records a gradual improvement in oxygen levels, initially in shallow-water habitats, and a reoxygenation of the water column, as cooler oceans became less stratified. Cool-water groups flourished in the aftermath of the extinction in cooler, Famennian oceans. Cooling ultimately led to Famennian glaciation in the southern hemisphere.
- the ultimate cause of the extinction remains rather elusive, although volcanism is a likely candidate. Submarine volcanism may account for several features of

this model, including global warming, and sea level rise. Terrestrial volcanism may also account for the suggested extinctions amongst land plants. Seismic data from the Pripyat-Dniepr-Donets rift system of Ukraine demonstrate rifting and intense volcanic activity during the Late Devonian, with two major phases of activity occurring, at the end of the Frasnian, and again at the end of the Famennian (Wilson and Lyashkevich, 1996). Recently, Courtillot and Renne (2003) have described remnants of a potential large igneous province, the “Viluy traps” in Siberia. Kimberlite pipes are evidence for an early, violent phase of volcanism, and Courtillot and Renne (2003) suggest that these pipes may be all that remains of a major continental flood basalt that caused the F-F extinction. At present this evidence has not been dated more accurately than 377-350 Ma, but future work may constrain this date to the late Frasnian. Courtillot and Renne (2003) point out the correlation between other large igneous provinces and mass extinctions (Fig. 9-7), and volcanism provides a viable causative source for the Frasnian-Famennian crisis.

9.5. Future work

Several areas which would benefit from future research have been touched upon in this thesis. A better understanding of the anoxic event in shallow water environments would help to clarify the role of anoxia in the extinction. No such sections were available for study in my field areas in North America, and little has been reported in the literature. Almost all sections in this study and in the published literature are constrained to tropical latitudes. It would be valuable to have further data from higher latitudes, as this would again help to constrain the extent of anoxia during the Frasnian, and would also improve data regarding the selectivity of the extinction.

The Canning Basin in Australia appears to be an intriguing field area, with several biostratigraphically complete F-F boundary sections, which now have accurate conodont dating. Previous authors have argued against the global anoxia hypothesis on the basis of the Canning Basin recording oxygenated conditions at the boundary. However, this study has shown that a detailed, combined geochemical, pyrite petrographic and microfacial analysis may show that anoxia developed in sections previously thought to have been oxygenated (e.g. in Nevada and Utah). Such a study has never been conducted in the Canning Basin, and may yet extend the global range of anoxia further.

Several studies have provided valuable, but incomplete, information. For instance, there is still little control on the terrestrial effects of the extinction. The sulphur isotope

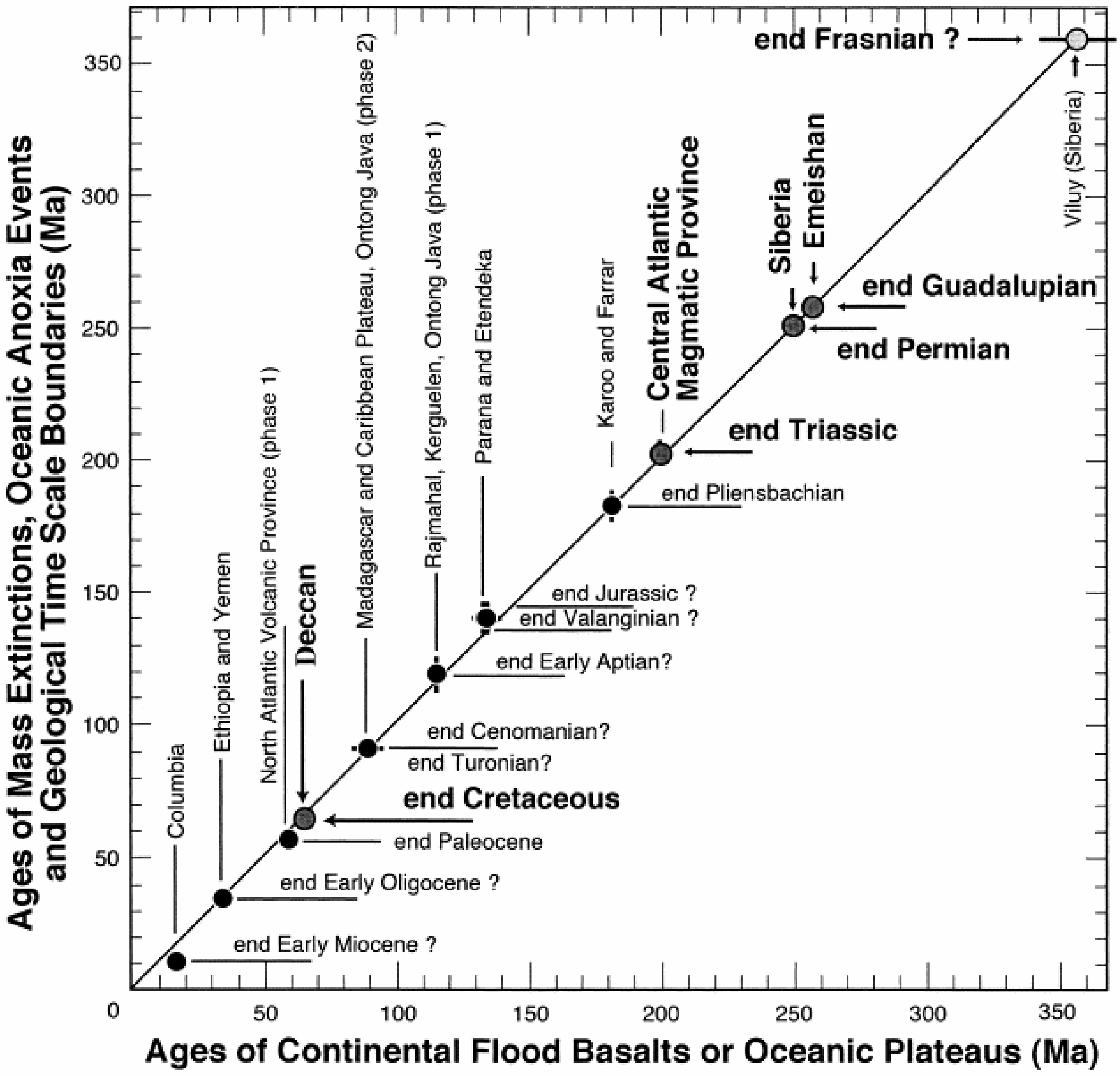

Figure 9-7: Correlation between large igneous provinces (continental flood basalts and oceanic plateaus), oceanic anoxic events, and mass extinctions (from Courtillot and Renne, 2003). The four most recent mass extinctions and corresponding traps are shaded dark grey. The F-F Viluy traps are currently been radiometrically dated.

studies of Goodfellow *et al.* (1989) were restricted to Canadian sections and should be followed up elsewhere.

The major, unanswered question, remains that regarding the ultimate cause of the extinction: anoxia may have been the proximate kill mechanism, but what led to widespread anoxic conditions? As mentioned above, some authors have suggested a causal link between volcanism and mass extinction and / or oceanic anoxia (e.g. Sinton and Duncan, 1997; Courtillot and Renne, 2003). This causal link, if it exists at all, is not clear, but Sinton and Duncan (1997) suggested that hydrothermalism, associated with large ocean plateau volcanic eruptions, resulted in global oceanic anoxia at the Cenomanian-Turonian boundary via two mechanisms: firstly, dissolved oxygen may have been consumed by the oxidation of magmatic sulphides and reduced metals present in hydrothermal effluent; secondly, through an increase in primary productivity brought about by an influx of hydrothermal Fe into surface waters. These two mechanisms are inferred to have lowered oceanic oxygen levels sufficiently far as to promote the widespread formation of organic-rich sediments (Sinton and Duncan, 1997). The processes by which submarine volcanism may lead to oceanic anoxia are possibly complex, and certainly worthy of further research, as volcanism near the F-F boundary provides a plausible, entirely earth-bound cause for the Late Devonian extinction. However, the extent of volcanism, either submarine or terrestrial, during the Devonian is currently poorly constrained. Courtillot and Renne (2003) identified the “Viluy” traps in Siberia, which have been dated to within approximately 15 my. of the F-F boundary. The search for other evidence of late Frasnian volcanism may yet yield more conclusive, and better-dated results, and this is a crucial area for future work.

This work has gone some way to emphasising the important role of marine anoxia in the Frasnian-Famennian extinction scenario, but the ultimate cause of the extinction will be debated for many years to come, and we may never know exactly what happened during one of the biggest faunal crises in the history of the Earth.