Iridium Abundances Across the Ordovician-Silurian Stratotype

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Chemostratigraphic analyses in the Ordovician-Silurian boundary stratotype section, bracketing a major extinction event in the graptolitic shale section at Dob's Linn, Scotland, show persistently high iridium concentrations of 0.050 to 0.250 parts per billion. There is no iridium concentration spike in the boundary interval or elsewhere in the 13 graptolite zones examined encompassing about 20 million years. Iridium correlated with chromium, both elements showing a gradual decrease with time into the middle part of the Lower Silurian. The chromium-iridium ratio averages about 10^6. Paleogeographic and geologic reconstructions coupled with the occurrence of ophiolites and other deep crustal rocks in the source area suggest that the high iridium and chromium concentrations observed in the shales result from terrestrial erosion of exposed upper mantle ultramafic rocks rather than from a cataclysmic extraterrestrial event.

A MAJOR EXTINCTION OF MARINE INvertebrates occurred near the end of the Ordovician (about 440 million years ago). According to Sepkoski (*1*), the Ashgillian or terminal Ordovician extinction could have been the second most severe biological crisis in the Phanerozoic with about a 20% loss of diversity at the family level. Interest in major extinctions and their possible link with collisions of large asteroids and comets with the earth producing excess iridium, as proposed by Alvarez *et al.* (*2*) for the Cretaceous-Tertiary boundary, previously led Orth *et al.* (*3*) to examine whether the terminal Ordovician represented another example of mass extinction synchronous with a large impact event. Chemostratigraphic studies were performed on the Ordovician-Silurian boundary section on Anticosti Island, Quebec, Canada. This boundary on Anticosti Island is defined by a conodont extinction seen in a thin, laterally persistent clay bed within a shallow-water marine carbonate sequence. No iridium anomaly, shocked quartz, or spheroidal particles (microtektites) were observed.

Because the absence of impact signatures might be attributed to local preservation factors, such as highly variable erosion and depositional rates in shallow water, we decided to investigate a deep-water section where rates of deposition and erosion are low and relatively uniform. The section chosen was across the Ordovician-Silurian boundary exposed at Dob's Linn, Scotland (Fig. 1). This stratigraphic section includes the internationally recognized Ordovician-Silurian boundary stratotype (*4*). It was selected as the boundary stratotype because it contains a sequence of well-defined graptolite zones (*5*) and contains clear evidence of Late Ordovician graptolite extinctions above the anceps zone (Fig. 2). Between anceps and the overlying extraordinarius band the dicellograptids and most diplograptids become extinct. Only two genera persist into the persculptus zone where numerous biserial forms appear (*6*). The rarity of conodonts in the Dob's Linn sequence and of graptolites at Anticosti prohibits precise correlation between these two Ordovician-Silurian boundary sections.

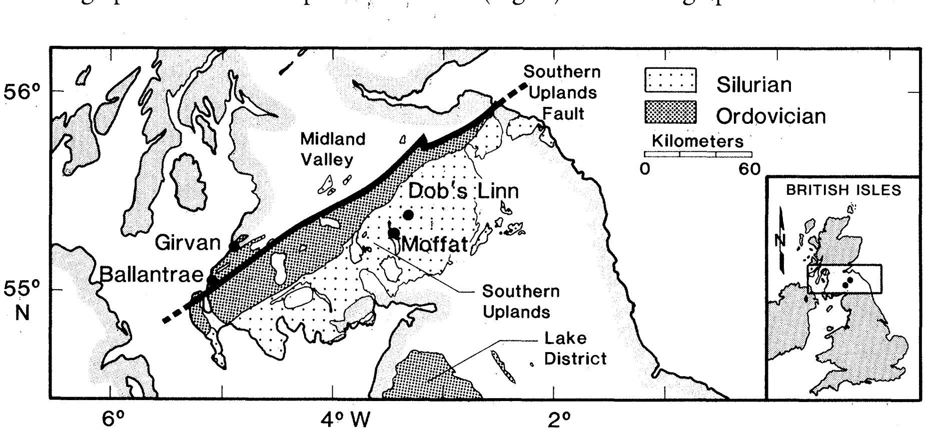

Fig. 1. Index map showing Ordovician-Silurian outcrops along the English-Scottish border [after Williams (*6*) and Owen in (*12*)]. The trace of the Southern Uplands Fault shows the approximate shoreline in the Upper Ordovician-Lower Silurian. The present Midland Valley were "highlands" in Moinian and Dalradian metamorphic rocks. The Silurian and Ordovician outcrop pattern shows the position of the depositional trough with Girvan near shore receiving proximal turbidity current deposits and Moffat and Dob's Linn apparently farther offshore at the toe of the submarine fans receiving sediments from the northwest.

The Dob's Linn section shows little lithologic variability and is characterized by black graptolitic shales, pale- and medium-gray mudstones, relatively thin metabentonite beds, and low carbonate content. Abundances for about three dozen elements (*7*) were investigated in 66 samples from the clingani zone (Late Ordovician) to the maximus zone (Early Silurian) at Dob's Linn. In 53 of the 66 samples, iridium concentrations were sufficient for more precise analysis. The iridium content in the entire section (Fig. 2) is relatively high, averaging about 0.120 ng of iridium per gram of sample compared to numerous other Paleozoic marine shales and mudstones. In these shales, iridium concentrations range from 0.02 to 0.120 ng/g and average about 0.050 ng/g. However, such values found at Dob's Linn are still as much as two orders of magnitude less than that found in the Cretaceous-Tertiary boundary interval (*8*). Correlation of iridium with other elements, except for chromium, was not found to be significant. Both chromium and iridium show relatively high concentrations, maintaining a ratio of Cr/Ir of about 10^6. Average concentrations, for both elements calculated for each graptolite zone increased with age (*9*). Chromium is associated with detrital rather than authigenic minerals in shales and mudstones (*10*). Iridium occurs in chromites, also with a Cr/Ir ratio of about 10^6 (*11*). The positive correlation of chromium with iridium at this ratio may reflect erosional contribution from chromium-bearing minerals.

Paleogeographic reconstruction of the Upper Ordovician and Silurian rocks of southern Scotland (*12*) shows the Dob's Linn section accumulating in a trough at the northern margin of the Proto-Atlantic or Iapaetus Ocean. The position of the trough is shown approximately by the Ordovician

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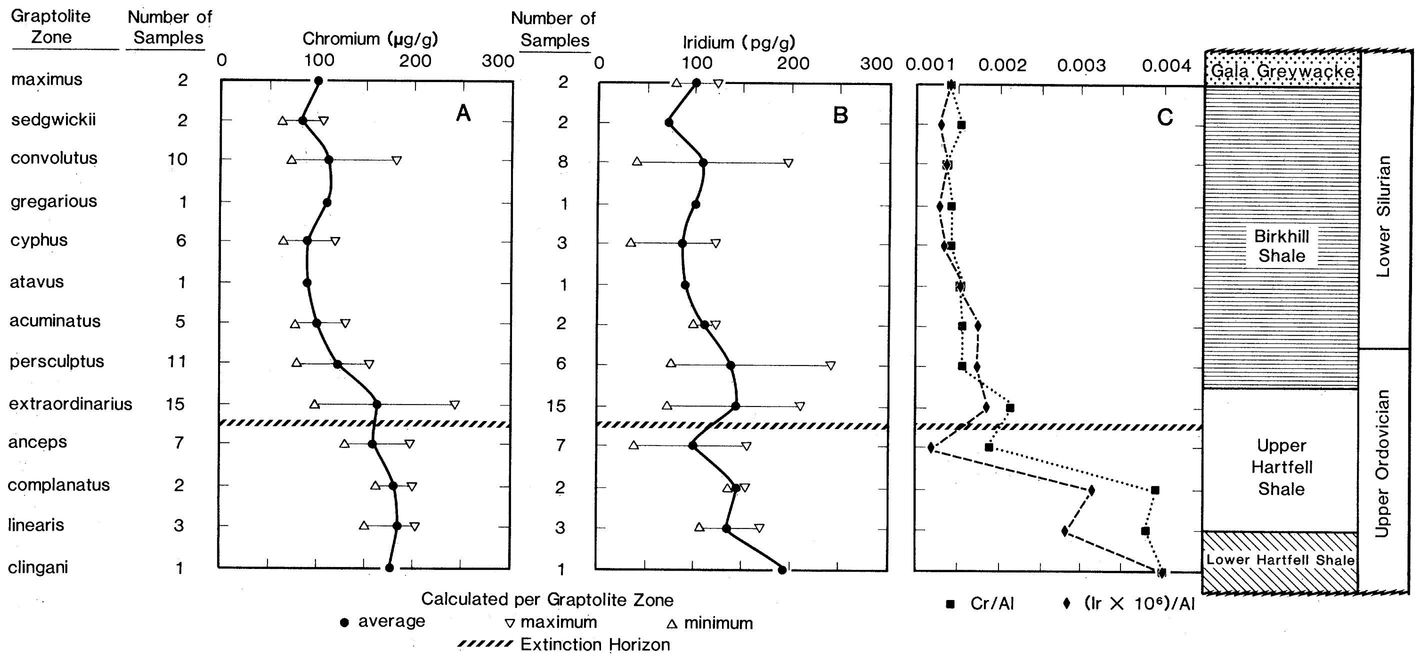

Fig. 2. Chemostratigraphy of chromium and iridium by graptolite zones at Dob's Linn, Scotland. Extinction horizon after Williams (*6*) and Berry *et al.* in (*7*). Ordovician-Silurian boundary was placed in 1985 at the base of the acuminatus zone by international agreement (*4*). (A) Chromium in micrograms per gram = 10^{-6} gram per gram. (B) Iridium in picograms per gram = 10^{-12} gram per gram. Iridium is reported in the figure in this unit rather than the more conventional nanograms per gram = 10^{-9} gram per gram to emphasize the consistency of the Cr/Ir ratio of 10^6 measured in this section. (C) Chromium and iridium averaged per zone normalized to average aluminum per zone. Aluminum is used as an indication of the nonmafic contribution to the sediment. This plot suggests that the major change in the relative proportion of the mafic to nonmafic contributions to the sediment occurred before the major extinction.

and Silurian outcrop pattern given in Fig. 1, with land to the northwest and deep water to the southeast.

An initial form of the trough developed in the Late Cambrian–Early Ordovician during the complex Caledonian tectonic events that deformed and metamorphosed earlier sediments to produce uplifted areas north of the trough. Obduction of oceanic crust onto the continental block as far south as the Southern Uplands Fault is indicated by the occurrence with these metamorphosed sediment of ophiolites with eclogites, serpentinites, gabbros, and blue schists in Arenig (Lower Ordovician) rocks near Girvan (*13*). Such rocks with a probable deep crustal or even upper mantle origin (*14*) are potential sources for high chromium and iridium values.

Deposition of flysch and shales continued as the oceanic trough redeveloped in the mid-Ordovician. At Girvan, thick turbidite sequences were deposited on deep-sea fans. Farther offshore at Moffat (Dob's Linn), at the toe of the fans, the rate of sedimentation was much less and only shales and mudstones were deposited.

The low rate of deposition of graptolite-bearing shales and mudstones (*15*) continued through the Ordovician-Silurian boundary interval with the source of detrital material being to the north from the Southern Uplands. By Wenlock time in the mid-Silurian, a volcanic arc (Cockburnland) had developed to the southeast of Dob's Linn so that a southern source now could feed sediments into the trough. Accordingly, the high iridium concentrations at Dob's Linn may be the result of continued erosion of the obducted deep crustal material exposed in the Southern Uplands and transported by turbidity currents into the trough. The gradual decline in both chromium and iridium values with time suggests reduction in the ultramafic source area or consumption of this source with the introduction of and dilution with normal basaltic material from the growing island arc developing to the southeast.

The average sedimentation rate in the analyzed section is about 4 m per million years (m.y.) (*15*). The average accumulation rate of iridium (average concentration of 0.120 ng/g), assuming an average initial sediment density of 2 g cm^{-3}, then is about 95 ng cm^{-2} $m.y.^{-1}$. For comparison, Kyte and Wasson (*16*) measured about 30 ng cm^{-2} $m.y.^{-1}$ averaged over 8 m.y. in Pliocene red clay from the mid-Pacific. In older sections (30 to 60 m.y.) from the same core, Kyte (*17*) found 13 ng cm^{-2} $m.y.^{-1}$, which is about twice the iridium value of 7 ng cm^{-2} $m.y.^{-1}$ reported by Barker and Anders (*15*) for modern worldwide micrometeoritic contribution of iridium. If 13 ng cm^{-2} $m.y.^{-1}$ represents an upper limit to the average accretion rate of iridium from micrometeorites in the Phanerozoic, then conservatively, greater than 80% of the iridium in the Dob's Linn section must have originated as detritus from land. The organic-rich graptolitic shales, especially those common in the anceps zone, contain somewhat lower iridium concentrations than the adjacent metabentonites and mudstones-shales, suggesting dilution of the detrital chrome-bearing minerals.

The lack of an iridium spike near the major extinction and the persistence of high but declining iridium values throughout the boundary interval, related to the local terrestrial, albeit, ultramafic source indicate that an extraterrestrial source is not required. The persistence of high concentrations of iridium and chromium over the measured section across the boundary can be attributed to detritial ultramafic material with a small contribution from micrometeorites because of the low rate of deposition at this location. None of the iridium chemostratigraphy found at Dob's Linn should have any obvious influence on extinctions. The cause, or causes, of the Late Ordovician extinctions remain to be determined, but might be related to nontectonic events such as the global Late Ordovician glaciation (*18*). Chemostratigraphic studies evaluating the relations among more chemical elements at Dob's Linn and at other deep-water Ordovician-Silurian boundary sections elsewhere, such as in China (*19*), may help resolve this question.

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Melittin-Like Peptides from the Shark-Repelling Defense Secretion of the Sole *Pardachirus pavoninus*

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Three ichthyotoxic peptides, pardaxins P-1 to P-3, have been isolated from the defense secretion of the sole *Pardachirus pavoninus*. Pavoninins, the steroid glycosides with shark-repelling ability, had previously been isolated therefrom. Each pardaxin consists of 33 amino acid residues having a distinctly hydrophilic carboxyl terminal region and a predominantly hydrophobic remainder; the pardaxin is thus strongly surfactant. These peptides show marked physical and pharmacological similarities to melittin, the major active constituent of bee venom, yet they lack sequence homology. They are probably also responsible for the predator-repelling property of the sole.

SOLES OF THE GENUS *PARDACHIRUS* secrete toxic material from the peculiar mucous glands that line their dorsal and anal fins (*1*). In addition to being ichthyotoxic and hemolytic (*2*), the crude secretion of *Pardachirus marmoratus*, Moses sole in the Red Sea, protects the fish from shark attacks (*3, 4*); the secretion of *P. pavoninus*, peacock sole in the western Pacific, presumably does the same (*1*). We have shown that groups of steroid monoglycosides, pavoninins from *P. pavoninus* and mosesins from *P. marmoratus*, are responsible in part for the toxicity and shark-repellent activity of the secretions (*5*).

On the other hand, Primor *et al.* reported isolation of pardaxin, an ichthyotoxic protein from the secretion of *P. marmoratus* (*6*), but its complete amino acid sequence has not been reported. We report here the isolation and primary structures of three toxic peptides from the secretion of *P. pavoninus*. These peptides are nearly identical to pardaxin (*7*), and therefore have been named pardaxins P-1 to P-3, where P refers to the species name.

Five *P. pavoninus*, averaging 20 cm in length, were captured along sandy areas near coral reefs around Ishigaki Island, Ryukyu Archipelago, Japan. We expressed the toxic secretion from the fish once daily over a 4-day period beginning on the first day of capture by placing the live fish in a shallow pan and pressing lightly along the base of their dorsal and anal fins. The collected secretion was stored frozen until lyophilization, which yielded 27 g of crude material including an undetermined amount of sea salt. Typically, 1 g of this material was twice precipitated from 10 ml of 0.1*M* acetic acid or 0.1*M* ammonium hydroxide by slow addition of 100 ml of cold acetone. This procedure produced a precipitate (420 mg) that was free of pavoninins—lipophilic active factors with shark-repellent activity (*5*)—and yet was ichthyotoxic and hemolytic. Incubation of the precipitate with chymotrypsin destroyed the activity, demonstrating the peptidic nature of the active components.

The ichthyotoxic factor in the precipitate

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