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Multiple Ir anomalies in uppermost Triassic to Jurassic-age strata of the Blomidon Formation, Fundy basin, eastern Canada

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ABSTRACT

A detailed profile of Ir concentrations in continental strata of the Blomidon Formation ostensibly spanning the Triassic–Jurassic boundary confirms the existence of multiple anomalies, with a peak Ir concentration of 450 pg/g. The total amount of Ir deposited exceeds 4 ng/cm^2, a value that requires an external source other than typical terrestrial sediment. Of the 10 other elements measure, only Zn and organic carbon are correlated to Ir. The organic carbon appears to be concentrated in mm-thick kerogenous laminae in greenish-grey to dark grey sediment layers that also host the Ir anomalies. The stratigraphic distribution of Ir and probably Zn appears to be controlled largely by redox boundaries conditions, with Ir probably forming organo-metallic complexes. We find no specific geochemical or sedimentological evidence for an extraterrestrial source for this enrichment, although we cannot exclude an impact origin. However, the close spatial and temporal relationship of the Ir anomalies in the Fundy and Newark basins to the basalts of the Central Atlantic Magmatic Province suggests alternative working hypotheses. Potentially, the volcanic rocks sourced the Ir through post-eruptive fluid mobilization into the surrounding sediments. Conversely, mantle outgassing and aerosol deposition during early stages of the eruptions may have been the source for the Ir anomalies. At this time, the data are insufficient to eliminate any of these hypotheses conclusively.

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1. Introduction

The nature of the biotic events surrounding the Triassic–Jurassic boundary remains somewhat enigmatic. It has long been argued that this system boundary coincided with a single, catastrophic extinction that places it among the “big five” extinction events of the Phanerozoic (Newell, 1963; Hallam, 1981, 1990; Raup and Sepkoski, 1982, 1984; Olsen et al., 1987, 2002a,b; Raup, 1992; Sepkoski, 1996, 1997; Pálfy et al., 2002; Whiteside et al., 2007). More recently, the latest Triassic has come to be regarded by many as an interval of accelerated turnover and decreasing diversity, potentially punctuated by several discrete extinction events (Hallam, 2002; Lucas and Tanner, 2004; Tanner et al., 2004). Nonetheless, a biotic event of some considerable magnitude occurred at the system boundary that severely reduced some faunal groups, and eliminated others that were already in serious decline. For example, the Rhaetian–Hettangian boundary marks the loss of the choristocerid ammonoid lineage (Guex et al., 2004), about 60% of latest Triassic radiolarian genera (Carter and Hori, 2005), and the last remaining conodonts (Aldridge and Smith, 1993). Tanner et al. (2004) reviewed potential forcing mechanisms and concluded that multiple processes operating during the latter part of the Triassic likely contributed to this complex biotic record. Gradualistic processes, such as the Rhaetian–Hettangian regressive–transgressive sequence, and the Late Triassic aridification of the Pangaean interior likely contributed to long term declines in both marine and terrestrial realms. Conversely, catastrophic processes, such as the eruptions of the Central Atlantic Magmatic Province (CAMP), or a hypothetical bolide impact may have forced the discrete extinction events that punctuate this record.

Olsen et al. (1987) proposed the bolide impact hypothesis to explain extinctions at the system boundary on the evidence of a Late Triassic age for the Manicouagan impact structure. This hypothesis was seemingly discounted when the age of the structure was firmly established at 214±1 Ma (Hodych and Dunning, 1992) and later confirmed at 215.5 (Ramezani et al., 2005). This is substantially older than the age of the Triassic–Jurassic boundary, previously accepted as 199.6±0.4 Ma (Ogg, 2004), but now proposed as 201.58±0.17 Ma (Schaltegger et al., 2008). Furthermore, reports of impact-derived materials from the system boundary have been conspicuously lacking; shocked-metamorphosed quartz grains were described from multiple levels at a section in northern Italy (Bice et al., 1992), but corroborating evidence has not been presented, and there have been no other verifiable reports of impact ejecta for the latest Triassic. Specifically, studies by Mossman et al. (1998) and Olsen et al. (2002b) of the strata at the system boundary in the Fundy and Newark basins failed to find impact materials. Nonetheless, discussion of the impact hypothesis was reinvigorated when Olsen et al. (2002a,b) published data that

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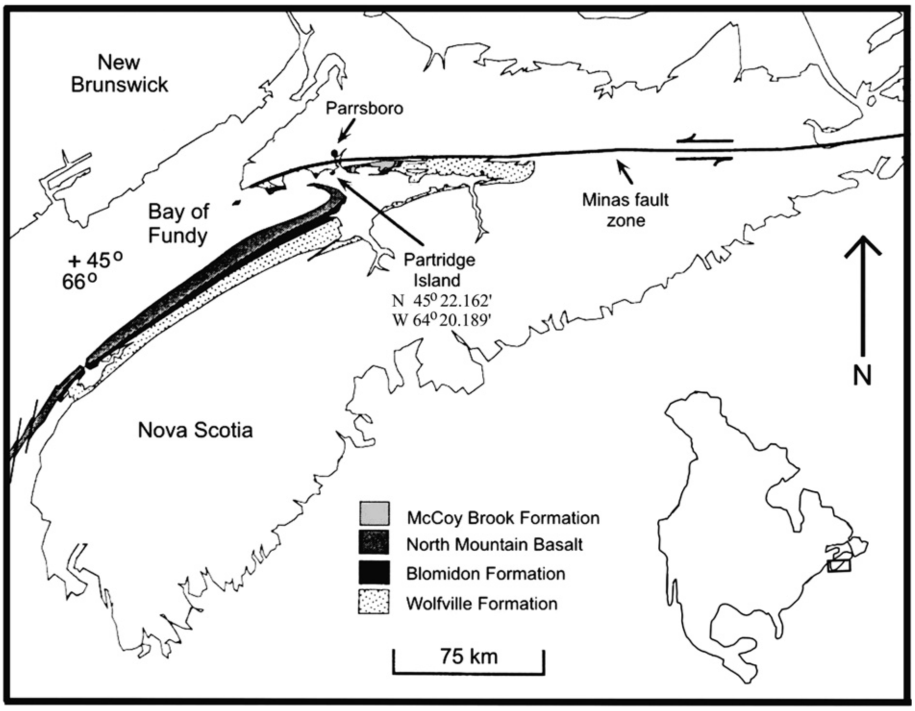

Fig. 1. Location and geologic map of the study area in the Fundy basin. Samples analyzed in this study were collected from Partridge Island, near Parrsboro, Nova Scotia (adapted from Tanner and Kyte, 2005).

showed elevated levels of Ir in several correlative sections in the Newark basin at a stratigraphic level interpreted as the Triassic–Jurassic boundary from palynological data. Although the maximum Ir concentration measured in these sections (285 pg/g) is one to two orders of magnitude below levels measured at the K–T boundary (e.g., Frei and Frei, 2002), the anomaly coincides stratigraphically with a high concentration (up to 80%) of "fern-like" (i.e. trilete) spores, drawing comparisons to the K–T impact scenario.

Earlier studies by Orth et al. (1990) (later republished by Mossman et al., 1998) found an Ir level of 150 pg/g in a single sample from the uppermost strata of the Triassic- to Jurassic-age Blomidon Formation of the Fundy basin. However, analyses by these authors of samples from sections spanning the Triassic–Jurassic boundary in Austria and Great Britain failed to identify an Ir anomaly. Mossman et al. (1998) also reported a modest Ir enrichment in the upper Blomidon Formation, but the sensitivity of their measurements were not adequate to resolve an anomaly at the resolution of the 150 pg/g reported by Orth et al. (1990).

Relevant to these studies, Tanner (2006) reported that Ir levels in samples from the base of the Blomidon Formation are below detection limits, thereby establishing that background levels in the formation are low.

Significantly, the studies of Orth et al., 1990 and Mossman et al., 1998 lacked close sampling resolution and were not constrained by the palynostratigraphic placement of the Triassic–Jurassic boundary in the Fundy basin. Tanner and Kyte (2005) performed the first high-sensitivity Ir analyses of samples from the Blomidon Formation, although on a limited sample set, which indicated that Ir enrichment (up to 310 pg/g) occurs in Fundy basin sediments at a stratigraphic level similar to that in the Newark basin. In contrast to the Newark basin, however, these new data indicated that the enrichment occurs at multiple levels in proximity to the boundary, rather than at a single horizon, and that this distribution is potentially controlled by the local concentration of organic matter in the strata. The small sample set could not resolve the structure of this anomaly, so in the present study we have analyzed the trace element geochemistry of a suite of 46 samples including most of a 100 cm interval of the Fundy basin

Fig. 2. Uppermost strata of the Blomidon Formation at Partridge Island comprise interbedded red and grey to dark grey mudstones. The contact with the North Mountain Basalt is covered by colluvium near the top of the image. The scale (arrow) is 20 cm.

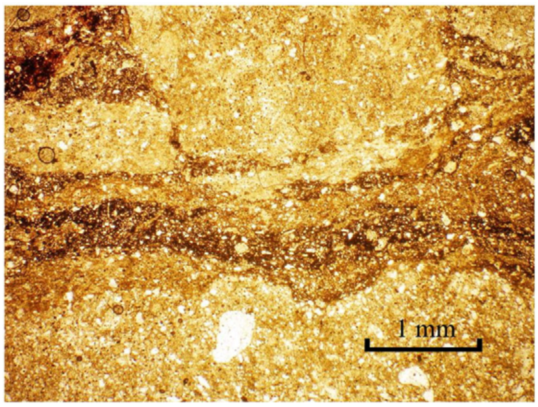

Fig. 3. Silty mudstone with stray sand grains and dark organic-rich (kerogen) laminae from sample at 42 cm in the section in Fig. 4, photographed in plane-polarized light. Kerogenous laminae range in thickness from 0.2 to 1.0 mm in this view (scale bar = 1.0 mm).

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section. Additionally, we explore mechanisms to explain the observed elemental patterns and discuss potential sources of the Ir enrichment.

2. Geologic setting and stratigraphy

The Fundy basin formed by the Middle Triassic as a terrestrial rift valley that filled with mostly red-bed sediments and tholeiitic basalts at least into the Early Jurassic (Fig. 1). During this time the basin drifted from 15°N to 26°N paleolatitude (Kent and Tauxe, 2005). In outcrop, the Blomidon Formation of the Fundy Group comprises 200 to 300+ m of cyclically interbedded sandstone and mudstone interpreted as the record of deposition in playa, sandflat, lacustrine, eolian and fluvial environments during an interval of semi-arid to arid climate (Tanner, 2000). The age of the formation is Late Triassic (Norian) to possibly Early Jurassic (Hettangian) (Kent and Olsen, 2000), and it is overlain by the North Mountain Basalt, dated at 201.3±0.3 Ma (Schoene et al., 2006).

The Blomidon Formation comprises mostly red mudstones and sandstones, with grey to nearly black mudstones interbedded with the red mudstones only in the uppermost meter (Fig. 2). This uppermost meter comprises beds of red mudstone that are 2 cm to 15 cm thick and grey mudstones that vary from light greenish-grey beds 2 cm to 5 cm in thickness to finely laminated beds. The non-laminated mudstones generally consist of an assemblage of silt to sand-size detrital grains with a sublitharenitic composition, a minor component of comminuted organic debris, and patchy micritic to sparry calcite cement. Laminated mudstones contain fine (mm-scale or finer) dark grey to black organic-rich laminae, interlayered with light grey to red mudstone laminae (Fig. 3). Calcite cement is locally abundant at several stratigraphic levels, resulting in nodular weathering of the mudstone. As reported by Tanner and Kyte (2005), the clay fraction of the mudstones comprises mostly illite, smectite and chlorite, with lesser amounts of kaolinite and mixed-layer clays. The relative proportions of the clay minerals do not vary appreciably through the uppermost meter of the section.

The placement of the system boundary in the Blomidon Formation is based on an abrupt transition of palynomorphs, from a Late Triassic assemblage dominated by *Patinosporites densus* and *Corollina torosus*, to a low diversity assemblage very strongly dominated by *C. meyeriana* (Fowell and Traverse, 1995). This palynological turnover event is similar to that

Table 1
Elemental data obtained by NAA (trace elements) and combustion analysis (organic carbon)

Top	Base	Sc	Cr	Fe	Co	Ni	Zn	Cs	Ce	Eu	Tb	Yb	Hf	Ta	Th	Ir	LOI	Corg
(cm)	(cm)	(μg/g)	(μg/g)	(mg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(pg/g)	(wt.%)	(mg/g)
0	2	9.3	41	23	12	30	38	4.3	31	0.94	0.6	1.4	4.1	0.7	17.9	49	10.8	1.0
2	4	13.5	70	39	18	39	73	8.0	62	1.02	0.8	2.5	3.3	1.0	12.1	111	7.5	0.8
4	6	9.6	49	24	12	31	44	5.9	67	1.06	0.7	2.3	4.9	0.9	9.7	110	7.1	0.5
6	8	10.6	54	36	13	53	62	6.1	125	2.01	1.3	3.6	6.9	1.1	11.3	83	6.8	0.5
8	11	10.8	56	35	13	25	92	6.4	91	1.48	1.0	3.3	8.4	1.1	9.8	91	5.7	0.6
11	12	12.1	66	51	16	44	159	8.5	89	1.42	0.9	3.0	5.1	1.0	9.8	239	7.6	0.4
12	13	12.4	70	39	15	26	246	8.6	92	1.46	1.0	2.7	4.8	1.0	9.4	254	10.4	0.9
13	16	7.8	43	21	9	38	182	5.2	57	1.09	0.7	1.8	3.2	0.7	6.3	273	18.2	0.7
16	18	9.6	60	33	10	40	150	6.0	62	0.97	0.7	2.3	4.4	0.8	7.8	71	16.4	0.6
20	22	8.8	58	29	10	29	79	5.2	51	0.99	0.7	2.3	4.8	0.8	7.6	52	13.0	0.9
22	23	9.3	62	27	10	22	172	5.5	70	1.15	0.8	3.0	8.4	1.0	9.7	118	12.7	0.8
23	25	6.8	49	21	7	32	34	3.6	59	1.45	0.9	2.6	6.2	0.6	6.7	71	19.4	0.9
25	26	8.2	57	25	9	33	46	4.4	57	1.34	0.9	2.7	6.7	0.8	7.6	58	14.5	0.7
26	27	9.1	66	26	10	23	46	5.2	57	1.11	0.8	2.7	7.6	0.9	8.7	39	11.5	0.6
31	32	7.5	53	22	8	18	38	4.1	54	1.30	0.8	2.4	5.8	0.7	7.1	37	16.4	ND
32	34	7.9	54	22	8	19	134	4.2	52	1.18	0.8	2.5	5.6	0.8	7.5	39	13.7	0.9
34	35	8.7	59	23	9	38	240	5.1	55	1.16	0.8	2.4	5.6	0.8	7.6	50	14.3	1.0
35	36	8.6	54	22	8	31	272	5.2	58	1.25	0.9	2.5	5.5	0.8	7.7	56	15.5	0.8
36	37	8.9	60	24	9	18	138	5.2	53	1.12	0.8	2.4	5.9	0.9	8.1	43	13.7	0.9
37	38	8.2	55	23	8	28	134	5.0	53	1.08	0.8	2.5	5.9	0.8	7.8	52	14.4	0.8
38	39	9.7	60	25	10	35	261	6.4	59	1.20	0.8	2.6	4.8	0.9	8.4	92	16.1	1.0
39	40	9.6	57	26	10	31	339	6.8	60	1.25	0.8	2.3	3.6	0.8	7.8	82	15.9	0.9
40	41	10.8	72	28	10	26	106	7.2	59	0.95	0.8	3.0	7.2	1.0	10.3	118	9.2	2.3
41	42	13.3	81	28	12	28	526	9.1	73	1.36	0.9	2.7	5.1	1.1	11.2	449	11.3	4.7
42	43	11.4	68	26	11	17	613	7.4	66	1.13	0.8	2.5	5.8	1.0	9.7	279	11.7	5.0
43	44	9.4	52	23	9	32	374	6.2	81	1.60	0.9	2.4	5.6	0.9	7.9	257	12.0	1.3
44	45	10.1	56	33	11	41	253	6.6	68	1.24	0.9	3.1	7.6	1.1	9.3	69	6.8	0.5
45	46	11.1	63	39	13	58	414	7.4	66	1.13	0.8	2.8	8.4	1.1	10.2	42	4.1	0.9
47	48	13.6	74	37	16	30	182	10.1	68	1.29	0.9	2.7	4.6	1.1	10.4	102	8.5	1.1
49	51	13.0	72	29	13	27	207	8.6	77	1.37	0.9	2.7	4.8	1.0	10.0	97	10.5	2.3
51	52	12.8	71	26	13	54	208	7.7	90	1.59	1.0	2.7	6.4	1.1	10.4	157	8.7	2.5
52	53	11.1	63	30	11	30	139	7.3	78	1.32	0.8	2.8	8.0	1.1	9.9	65	6.7	0.5
53	55	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	40	5.8	0.3
56	58	10.0	55	33	10	30	110	6.2	68	1.28	0.9	3.0	7.4	1.1	9.2	53	5.9	0.2
60	61	9.7	54	34	10	37	102	5.8	66	1.23	0.8	2.7	8.9	1.1	9.2	37	5.7	0.3
69	70	12.7	70	43	14	39	110	8.6	75	1.33	0.9	2.7	5.9	1.1	10.1	63	1.2	0.4
70	71	12.1	69	28	12	26	200	7.9	77	1.38	1.0	2.6	6.1	1.0	9.8	86	8.1	2.8
71	72	11.6	66	22	11	33	230	6.6	99	1.58	1.1	2.5	6.7	1.1	11.5	320	9.1	1.5
73	74	9.9	56	26	10	22	59	6.1	69	1.19	0.8	2.8	10.4	1.1	10.7	38	5.8	0.4
79	80	9.6	54	33	10	35	68	5.9	63	1.12	0.8	2.5	7.9	1.1	10.5	70	5.1	0.4
89	90	9.9	54	30	10	30	62	6.3	74	1.32	0.8	2.2	6.6	1.0	8.5	45	8.5	1.0
90	91	10.1	57	24	9	19	80	6.1	71	1.18	0.8	2.4	7.3	1.1	9.1	29	6.1	0.5
91	92	9.9	55	23	9	22	82	6.0	63	1.16	0.7	2.3	7.3	1.1	8.6	33	7.8	0.5
93	94	9.7	53	28	10	23	60	6.1	73	1.19	0.8	2.8	10.0	1.2	9.8	31	3.0	0.7
99	100	9.9	56	31	10	39	63	6.4	70	1.15	0.7	2.5	6.6	1.0	8.8	58	8.7	0.4
149	150	7.6	42	25	7	30	59	4.8	57	0.98	0.7	2.7	8.0	0.9	7.7	24	5.1	0.4

ND = no data due to machine failure.

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described in the Newark basin (Cornet and Olsen, 1985), and is the basis for placement of the Triassic–Jurassic boundary in that basin as well. In the Jacksonwald syncline of the Newark basin, the location of the sections analyzed by Olsen et al. (2002a,b), this turnover occurs approximately 8 to 12 m below the base of the Orange Mountain Basalt. At Partridge Island in the Fundy basin, the section analyzed by Fowell and Traverse (1995) and Tanner and Kyte (2005), this turnover occurs 20 to 30 cm below the base of the North Mountain Basalt (Olsen et al., 2005). The "fern spike" seen at the boundary in the Jacksonwald syncline has not been identified in the Partridge Island section.

We note, however, that this placement of the system boundary in the Newark Supergroup is not accepted universally. Lucas and Tanner (2007) cited ambiguities in the correlation of this continental palynological record to Tethyan sections, as well as some alternative correlations of the Newark paleomagnetic record to the marine. Consequently, these authors proposed that the palynological turnover in fact represents an older biotic event, perhaps the Norian–Rhaetian boundary.

3. Sampling and analytical methods

Tanner and Kyte (2005) examined the geochemistry of the uppermost 70 cm of the Blomidon Formation at Partridge Island, a tombolo on the north side of the Minas basin, near the town of Parrsboro, Nova Scotia. In that study, the section was analyzed by 5-cm channel sampling, i.e., removing individual samples that represented composites for 5 cm intervals. For this study, we re-sampled the uppermost Blomidon Formation at the same Partridge Island section at a resolution of 1 cm. The cliff-side section was trenched to expose a fresh rock surface at a location about 10 m up-dip from the sample site of the previous study (see Fig. 1 for GPS coordinates). Samples were removed in one-centimeter increments to create a continuous sample suite from the formation top (contact with the North Mountain Basalt) to a depth of 1.5 m below the top, although some samples were later combined for analysis.

For neutron activation analysis (NAA), a 1 g split of each sample was heated overnight at 105 °C and then ground to a powder in a high-

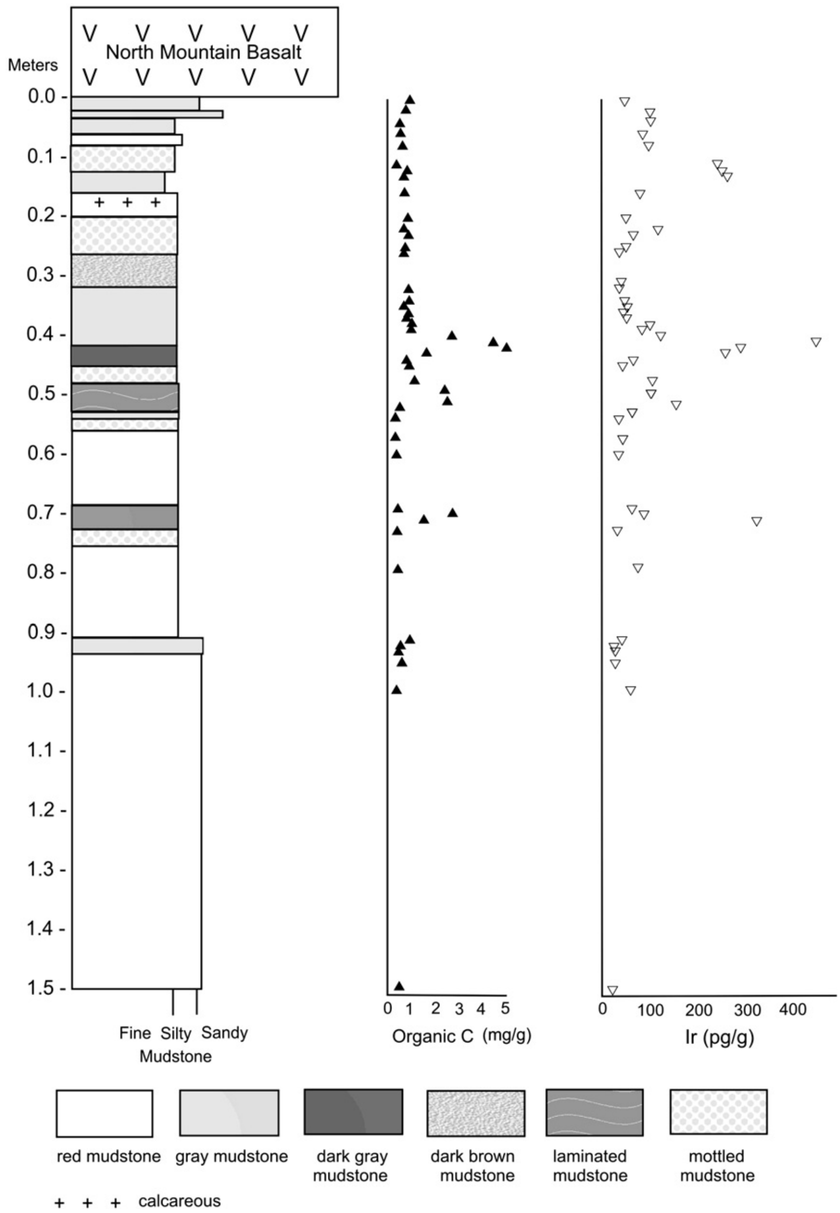

Fig. 4. Lithostratigraphy of the uppermost 1.5 m of the Blomidon Formation measured at Partridge Island with corresponding analyses of C_{org} (in mg/g), measured by combustion analysis, and Ir (in pg/g), measured by NAA (see Sampling and analytical methods).

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purity alumina mortar. Due to the high organic content, the powders were ashed by stepwise heating in quartz–glass crucibles to 100, 350, and 850 °C. This process oxidizes organic matter, decomposes carbonate and converts all Fe to Fe_2O_3. Mass loss due to this heating ranged from 1.2 to 19.4%, with an average of 9.7% and elemental concentrations have been corrected accordingly (Table 1). A ~200 mg split from each sample was sealed in a quartz–glass vial and irradiated for 30 h in the University of Missouri Research Reactor at a neutron flux of 5×10^{13} n cm^{-2} s^{-1}. Two months following the irradiation, sample powders were counted on coaxial intrinsic Ge gamma-ray detectors (with resolution from 1.75 to 1.90 keV at 1.3 MeV) to determine Sc, Cr, Fe, Co, Ni, Zn, Cs, Ce, Eu, Tb, Yb, Hf, Ta, and Th concentrations. Iridium was then chemically purified using a method similar to that described by Schellenberg et al. (2004) prior to counting. Typical 1-sigma counting errors for the NAA data are <10 relative percent, except for Ni which can be as high as 30%. Results of NAA are compiled in Table 1 with the top and base of each analyzed interval indicated in columns one and two.

A second sample split was analyzed for organic carbon content (C_{org}) in a Leco Truspec C/N(R). Samples were powdered and decarbonated in a 5% HCl solution for 2 h at room temperature, centrifuged, washed and dried. A foil capsule containing 0.1 to 0.125 g of the sample was combusted in a pure O_2 atmosphere at 950 °C, and the evolved CO_2 measured by an infrared cell. Results of these analyses are included in Table 1. Standard petrographic thin sections were prepared from ten samples and examined by standard optical microscopy.

4. Results

The results of these analyses confirm the earlier results (Tanner and Kyte, 2005) that Ir is enriched at multiple horizons in the uppermost meter of the Blomidon Formation at Partridge Island (Fig. 4). Levels of Ir vary in the section by more than an order of magnitude from a minimum of 24 pg/g at the base of the analyzed section (150 cm below the formation top) to a peak concentration of 449 pg/g at 42 cm. Most Ir concentrations are in the range of ~100 pg/g or lower, but eight samples have concentrations >150 pg/g. If we examine these data conservatively and consider only Ir concentrations >150 pg/g as anomalous, then we identify Ir anomalies at four levels: in three samples from 11–16 cm, in three samples from 41–44 cm, in a single sample from 51 to 52 cm, and in a single sample from 71–72 cm. Concentrations of C_{org} in the section also vary by over an order of magnitude, from a minimum of 0.2 mg/g to approximately 5 mg/g. In general, the C_{org} concentration corresponds to the rock color, with the highest concentrations occurring in dark grey mudstones or grey–red mottled mudstones that contain kerogen laminae (Fig. 4). Peak levels of C_{org} (above 1 mg/g) coincide quite clearly with elevated levels of Ir; e.g., the interval from 40 cm to 44 cm contains the maximum levels of both Ir and C_{org} in the section. The single prominent exception to this relation appears in the interval 11 cm to 16 cm, which has anomalous Ir but not high C_{org}, although we note that the mudstones in this interval are grey to mottled red–grey and contain kerogen laminae. Nevertheless, C_{org} and Ir for the entire section display a modest positive correlation ($r^2=0.40$; Fig. 5A). If we ignore the anomaly from 11 cm to 16 cm and consider only the samples from the section below 16 cm, the correlation between C_{org} and Ir is much more pronounced ($r^2=0.59$).

Among the other trace elements, Th alone has its peak concentration at the top of the formation, while the peak concentrations of Ce, Eu, Tb and Yb all occur 8 cm below the formation top, levels that do not correlate with enrichment of Ir or C_{org} (Fig. 6). Most of the trace elements analyzed vary in concentration by a factor of two to three, but Zn is notable in that it is the only trace element (other than Ir) to vary in concentration by more than an order of magnitude. Additionally, of all the elements measured, only Zn is moderately correlated with Ir ($r^2=0.42$; Fig. 5B). The samples with the highest Ir concentrations also have relatively high Zn, but not all high Zn samples have high Ir. The other elements measured exhibit no significant

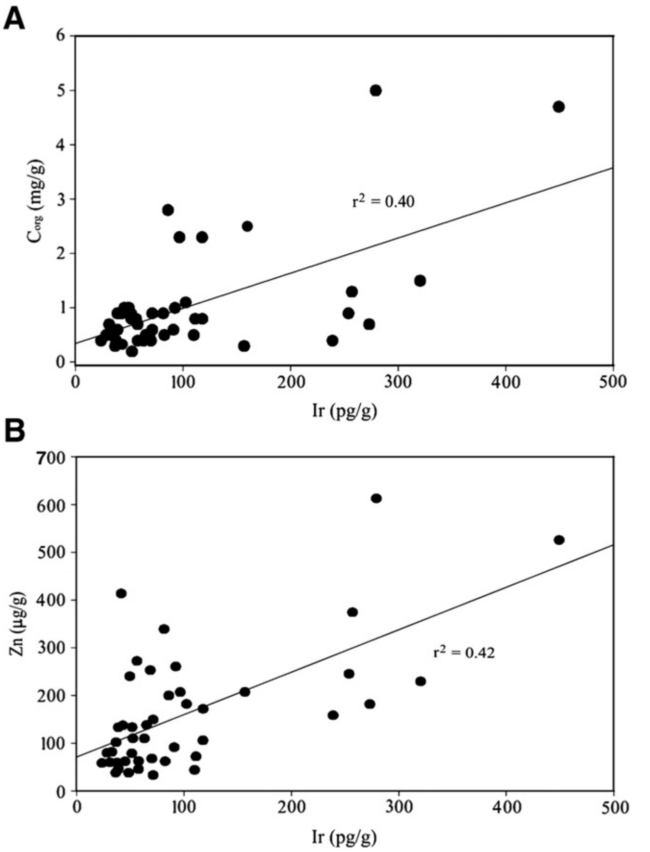

Fig. 5. Concentrations of A) C_{org} (determined by combustion analysis), and B) Zn (measured by NAA) plotted against Ir concentration, with lines of least-squares regression.

correlation with Ir. Zinc concentrations are also significantly correlated to C_{org} ($r^2=0.49$), showing the strongest correlation to bulk organic carbon of any element measured.

5. Discussion

5.1. Significance of the Ir anomalies

Although the peak concentrations of the Ir anomalies are small, they are comparable to anomalies at some sites known to contain impact ejecta, such as the late Eocene clinopyroxene (cpx) spherule deposits. At several localities where the late Eocene deposit has been positively identified, peak Ir concentrations are ≤250 pg/g (e.g., Sanfilippo et al., 1985; Keller et al., 1987). Rather than the peak Ir concentrations within a sediment, a better measure of an Ir anomaly is the fluence, or the total mass of excess Ir deposited per cm^2. If we assume an average background Ir concentration of 80 pg/g, and a dry bulk density of 2.2 g/cm^3, then the excess Ir in the eight samples with Ir concentrations >150 pg/g is 4.1 ng/cm^2. This is a non-trivial value and corresponds to about 9 mg cm^{-2} of chondritic matter (based on 465 ng/g Ir in CI chondrites; Lodders and Fegley, 1998). By comparison, estimates of the Ir fluences for the global impact deposits recognized for the late Eocene cpx-spherule layer and the K/T boundary are about 11 and 55 ng/cm^2, respectively (Kyte and Liu, 2002; Donaldson and Hildebrand, 2001). Clearly the Fundy basin Ir anomalies are significant and not typical of non-marine sediments. These anomalies require an external source for the Ir, other than typical detrital sediment.

5.2. Distribution of Ir and C_{org}

Based on the association with rock color, Tanner and Kyte (2005) concluded that the enrichments in the Partridge Island section are

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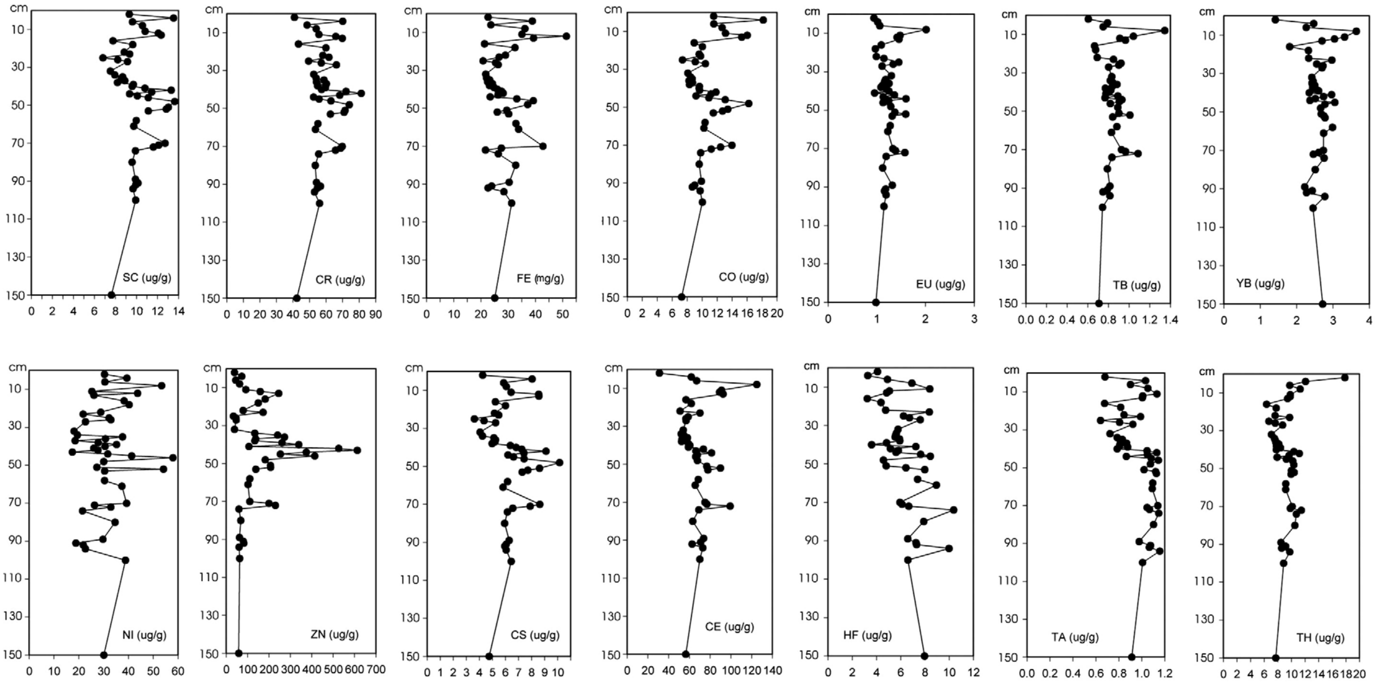

Fig. 6. Vertical distributions of individual trace elements listed in Table 1 for the stratigraphic section in Fig. 4.

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possibly related to the organic content of the sediments and suggested diagenetic remobilization and redox potential as a control for distribution of these elements. The mobility of Ir and other PGEs in the sedimentary environment was investigated by Colodner et al. (1992) who examined elemental response to redox conditions in a marine section at the K–T boundary. That study found that Ir is lost from oxic and transition zones, and concentrates preferentially in reduced sediments. Similarly, Wang et al. (1993) identified a global Ir anomaly at the Devonian–Carboniferous (D–C) boundary of similar magnitude as that we describe for the Partridge Island section. They found that the Ir anomaly was typically found at the base or the top of a widespread black shale unit, but never throughout the black shale. On the basis of inter-elemental ratios and a lack of impact materials, these authors cited redox redox-boundary conditions during deposition, or early diagenesis as a control for Ir concentration, and rejected an impact explanation for this anomaly. Conversely, Anbar et al. (1996) found no preference by Ir for anoxic environments in natural waters, but did suggest that Ir is stabilized by forming organo-metallic complexes. This supports the earlier work of Schmitz et al. (1988) that much of the Ir in the K–T boundary clay at Stevns Klint (Denmark), where Ir levels reach 35 ppb, is bound as organo-metallic complexes in kerogen. They found, conversely, that other trace elements (e.g., Fe, Ni, Co and Zn) are largely concentrated in sulfide spherules.

Our new data are consistent with the suggestion that Ir is bound as organo-metallic complexes in the kerogenous laminae in the grey and mottled mudstones. We noted above that the Ir concentration is anomalous in the interval 11 cm to 16 cm, where C_{org} is low, but petrographic examination demonstrates that kerogenous laminae are in fact present in the interval, but are exceedingly thin. Potentially, if the Ir is concentrated in a few of these lamellae, it might not correlate strongly with bulk C_{org} if the total amount of C_{org} in the sample is low. However, if the sediments are still reduced, a redox potential could still concentrate the Ir.

5.3. Source of Ir

Hori et al. (2007) published the first detailed geochemical data set for a deep marine section that spans the Triassic–Jurassic boundary. In bedded cherts of the Mino terrane, southwestern Japan, where the position of the system boundary is well constrained by radiolarian zonation and the final appearance datum of conodonts, the authors reported an increase in levels of PGEs in uppermost Triassic strata coinciding with the radiolarian decline, and a maximum Ir "anomaly" of 70 pg/g, about 25 cm below the interpreted position of the Triassic–Jurassic boundary. From the Pd/Ir ratio, the authors surmised that the PGE enrichment is derived from either flood basalt volcanism or a siderophile-rich impactor. They discounted a flood basalt origin, however, because the REE abundances are relatively constant throughout the section and resemble in profile the pattern for average continental shales. Furthermore, the authors inferred that a high mixing rate of basaltic debris would be required to account for the observed PGE concentrations. Thus, Hori et al. (2007) favored an impact origin for the PGE enrichment observed in this deep marine section, and assumed that impact melt mixed with the marine sediments at 2.5%. Curiously, however, no impact debris has been described in this section, but basaltic fragments are present, although not precisely at the same stratigraphic level as the peak Ir enrichment. Significantly, Hori et al. did not consider volcanic aerosols (e.g., Olmez et al., 1986) as a potential source of their Ir anomaly.

In general, we do not find the arguments of Hori et al. to be compelling. The Hori et al. anomaly is nearly an order of magnitude lower than in our samples and would not be distinguished from background levels in our samples. Terashima et al. (2002) noted that PGE concentrations in sediments tend to correlate negatively with sedimentation rates. Hence, PGEs tend to be enriched in deep marine sediments compared to continental or shallow marine sediments, making a concentration of 70 pg/g in the Japanese section unremarkable. Further, the PGE abundances (Ir, Ru, Pt, Pd) in their anomaly are not chondritic and appear more similar to their background samples than to extraterrestrial matter. We note that the Ir "anomaly" of Hori et al. (2007) occurs directly above a thin "red layer" with a Ce anomaly, and we suggest that a redox event might have concentrated PGEs in this horizon. Finally, given the difficulty of correlating the system boundary between continental and deep marine environments, we are unable to conclude that the anomaly of Hori et al. (2007) correlates to the Ir anomaly we observed in the Fundy basin.

Tanner and Kyte (2005) discussed possible origins for the PGE enrichments they observed in the continental sediments of the Fundy basin. Based on the inter-element ratios of the PGEs and the apparent lack of impact-derived materials, the authors suggested that an extraterrestrial origin for the PGE enrichment is unlikely. Specifically, the authors noted that ratios of Pd and Au to Ir exceeded the ratios for ordinary chondrites by an order of magnitude or more. However, of all the elements measured by Tanner and Kyte (2005), including Pd and Au, and those reported in this study, only Ir, and to a lesser extent Zn, are highly anomalous relative to typical concentrations expected for average upper continental crust, or shales (Lodders and Fegley, 1998). As a result, we would expect all element/Ir ratios to be greater than those in chondrites. Since the Zn/Ir ratio is three orders of magnitude higher than in CI chondrites (Lodders and Fegley, 1998), we also discount the possibility that the Zn has an extraterrestrial source. Zinc is most strongly correlated to Ir, however, so it is possible, or even likely that these elements have been concentrated by similar geochemical processes.

At this time, we cannot exclude an extraterrestrial source for the Ir anomalies, but neither can we present any strong evidence to support such a hypothesis. We find no direct evidence of impact spherules, a common component in known impact deposits (e.g., Kyte, 2002). A study of quartz grains in this section (Mossman et al., 1998), failed to find shocked quartz, but the presence of abundant detrital quartz in these sediments makes a search for traces of shocked quartz a nearly impossible task. Further, at such low Ir concentrations, equivalent to 0.1% of CI chondrite, application of chemical ratios (e.g., Ir/Cr, Ir/Pd) as a tracer for extraterrestrial matter in these sediments is impractical. This is because the estimated meteoritic component of elements that might be diagnostic for impact deposits, such as Ni, Cr, and Pd are overwhelmed by terrestrial contributions at such low abundances. Since the Cr in these sediments is clearly dominated by detrital sources, an attempt to measure a Cr-isotopic anomaly (e.g., Shukolyukov and Lugmair, 1998) would also likely fail. Only Os might also be expected to exhibit a similarly small anomaly. Potentially, sufficient Os could be extracted from these sediments to find an Os-isotopic anomaly, but even this would not be suitable for distinguishing between an extraterrestrial and a mantle source for Os (e.g., Luck and Turekian, 1983). Another potential tracer for extraterrestrial matter could be ^{3}He, if the deposition of extraterrestrial matter included high concentrations of interplanetary dust (e.g., Farley et al., 1998, 2006).

Perhaps if there were evidence that this Ir anomaly was global in extent, an impact hypothesis might garner greater consideration. However, at this point, attempts to find a global Ir anomaly have failed (Wang et al., 1993), and the occurrence of this anomaly is currently restricted to the localities within the Newark and Fundy basins, which are closely situated relative to the CAMP volcanics and separated by only ~1000 km.

The proximity of the sedimentary section in which we observe the anomalous trace element concentrations to the overlying North Mountain Basalt invites comparison between the two. Greenough and Fryer (1995) analyzed a broad suite of major and trace elements in 36 samples from a variety of lithologies in the North Mountain Basalt. We find no consistent relationship between our data and the composition of the North Mountain Basalt; i.e., some elements occur at comparable levels in both the sediments and the basalt (Ni, Tb, Yb Hf and Ir), while others are enriched in the sediments relative to the

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basalt (Zn, Cs and Th), and still others are depleted (Sc, Cr, Co and Ta). If these elements were remobilized from the overlying basalt, for example by hydrothermal fluids, the wide variation in the patterns of enrichment must result from significant differences in element mobility.

The distribution of zeolites in the North Mountain Basalt and the overlying McCoy Brook Formation attests to post-volcanic fluid flow in the Fundy basin (Kontak, 2008). Hence, the North Mountain basalt must be considered a potential source of the Ir in the Blomidon Formation, with concentration in the organic-rich sediments controlled by redox-boundary conditions during early diagenesis. In the Jacksonwald syncline, the Ir enrichment and proposed system boundary occur about 8 to 12 m below the basal flow of the Orange Mountain Basalt (Olsen et al., 2002a,b). Although there is no direct evidence for fluid mobilization associated with the igneous activity (e.g. widespread zeolite mineralization), as there is in the Fundy basin, we must consider the volcanics and intrusives of the Jacksonwald syncline as potential sources of Ir.

Tanner and Kyte (2005) suggested that mantle outgassing associated with the CAMP eruptions could potentially account for the anomalous elemental concentrations in these strata. As they noted, eruptions of ocean island basalts are known to emit high levels of Ir in aerosols (Sawlowicz, 1993); concentrations as high as 6.4 ng/g have been measured in aerosols at Kilauea, for example (Olmez et al., 1986), and 7.5 ng/g has been measured in sublimates at Reunion Island (Toutain and Meyer, 1989). Elevated trace element concentrations in sediments as a result of volcanic aerosol deposition could explain the apparently synchronous Ir enrichment over a broad region.

The enormous volume of the CAMP eruptions, 3×10^6 km^3 (Olsen et al., 2002b), could certainly be sufficient to produce a significant amount of Ir in aerosol form. Hypothetically, if the Ir fluence of 4.1 ng/cm^2 in Fundy basin was global in extent, this would translate to total Ir deposition of ~2×10^{10} g. At a concentration of 7 ng/g in outgassed volatiles (from the references above), this mass of Ir would be released by the eruption of ~6×10^{20} g of basaltic lava assuming 0.5% mass loss as volatiles, which would be contained in c. 2×10^5 km^3, a small, but significant portion of the estimated total volume of CAMP. But there are notable uncertainties inherent in this interpretation. Despite clear evidence that volcanic aerosols from ocean islands can have significant Ir concentrations, there are no data to prove that volcanic exhalations have resulted in Ir anomalies in sediments. Also, there are no data on the Ir content of continental flood basalt aerosols, but given the mantle origin for these eruptions, Ir-rich aerosols from CAMP are plausible. Finally, we have no data as yet that indicate that the Ir anomaly extends beyond the Triassic rift basins of eastern North America. Nevertheless, the potential for a significant Ir-rich plume beyond this region cannot be ignored.

The location of the horizon of enrichment below the lowest CAMP basalts in the Fundy and Newark basins is not an impediment to a volcanic aerosol origin for the Ir anomaly. Olsen et al. (2002a,b) estimated the time between the Ir peak/fern spike horizon and the eruption of the Orange Mountain Basalt at a modest 20,000 yr. Extensive dating of the CAMP basalts and associated intrusions documents that igneous activity began in some parts of the province before others (Marzoli et al., 2004; Nomade et al., 2007). Hence, the iridium enrichment and contemporaneous palynological turnover in the basins of the Newark Supergroup could have resulted from initiation of intense CAMP eruptive activity at another location. Thus, we offer this mechanism as an additional working hypothesis, although at this time we are unable to support it above the other hypotheses discussed above.

6. Conclusions

This study confirms earlier results that a number of Ir anomalies occur in the uppermost strata of the Blomidon Formation and that this enrichment occurs in stratigraphic proximity to a horizon of palynological turnover that has been interpreted as the Triassic–Jurassic boundary. Although the peak Ir concentrations are low, 449 pg/g, the total Ir deposited at this site is ~4.1 ng/cm^2, an amount that cannot be explained by normal sources in detrital sediments. The concentrations of Ir and Zn correlate with the concentration of organic carbon in the section. We attribute the specific patterns of enrichment to elemental remobilization and concentration at redox boundaries during early diagenesis. Iridium and Zn likely formed organo-metallic complexes in the kerogen laminae in the grey mudstones.

Given the lack of verifiable reports of impact debris at the Triassic–Jurassic boundary, and in particular from those sections where enrichment in Ir is documented, we do not support the hypothesis for an extraterrestrial source suggested by Olsen et al. (2002a,b) and Hori et al. (2007), although we cannot conclusively reject it. Given the close proximity of the Ir anomalies here and in the Newark basin to the very extensive CAMP volcanics, we suggest a local source for the anomaly. Remobilization of trace elements from the overlying North Mountain Basalt (in the Fundy basin) and the Orange Mountain Basalt (in the Jacksonwald syncline) by post-eruptive fluid movement is a potential source of the Ir observed in the underlying sedimentary strata. Finally, we consider as an additional hypothesis the scenario of regional deposition of Ir through volcanic aerosol deposition during the early stages of the CAMP eruptions. At this time, we are unable to discriminate among these multiple working hypotheses.

There are many lines of future research that could contribute to this problem. One obvious area of study would be to determine whether this anomaly extends to other Triassic rift basins, and whether detailed profiles like ours would demonstrate multiple anomalies as in the Fundy basin. If this anomaly could be found in marine sediments, it would provide a powerful chronostratigraphic tool to correlate terrestrial and marine sequences. Extending this anomaly into the marine realm could show whether this is a regional deposit, as might be expected for a volcanic source, or global in extent, which might favor an extraterrestrial event.

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