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Anomalous iridium enrichment at the Triassic–Jurassic boundary, Blomidon Formation, Fundy basin, Canada

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Abstract

We present new analyses that confirm Ir enrichment (up to 0.31 ng/g) in close proximity to the palynological Triassic–Jurassic boundary in strata near the top of the Blomidon Formation at Partridge Island, Nova Scotia. High Ir concentrations have been found in at least two samples within the uppermost 70 cm of the formation. Ratios of other PGEs and Au to Ir are generally higher by an order of magnitude than in ordinary chondrites. No impact-related materials have been identified at this horizon in the Blomidon Formation, therefore we cannot confirm an extraterrestrial source for the anomalous Ir levels. We consider, however, the possibility that regional basaltic volcanism is a potential source for the Ir in these sediments. The elevated Ir concentrations are found in reduced, grey colored mudstones, so redox concentration is a possible explanation for the distribution of Ir in these strata.

Keywords: Iridium; Triassic; Jurassic; Siderophile; PGEs

1. Introduction

The decline in diversity at the Triassic–Jurassic boundary (TJB) is generally regarded as one of the “big five” mass extinctions of the Phanerozoic, although recent studies now recognize that this decline took place in several stages culminating in the boundary extinctions [1–3]. Explanations for these extinctions have included such diverse hypotheses as long-term climate change, sea-level change, atmospheric effects of prolonged volcanic activity, bolide impact, and catastrophic greenhouse warming resulting from methane hydrate release (see review in [2]). Olsen et al. [4,5] reported data pertinent to this topic when they described a “modest Ir anomaly” at a zone of palynological turnover interpreted as the TJB in the upper Passaic Formation (Exeter Township Member) in the Jacksonwald syncline of the Newark basin. In four correlative sections they found an average peak Ir concentration of 0.14 ng/g and a single maximum of 0.29 ng/g. Although these Ir levels are one to two orders of magnitude smaller than the anomaly reported at the K–T boundary [6], they are several times greater than in typical upper crustal rocks [7], making their occurrence at the boundary noteworthy.

Significantly, the Ir enrichment in the Jacksonwald syncline section coincides closely with (but overlies slightly) a peak concentration (up to 80%) of trilete (i.e., fern-like) spores. Although they made no firm conclusion in regard to the origin of the Ir, Olsen et al. [5] found the correlation of the Ir, the fern spike

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and terrestrial mass extinction intriguing and suggested that it might be related to a bolide impact. However, the authors noted a lack of distinct correlation of the Ir concentration with the concentrations of other siderophile elements, such as Co, Ni and Cr that would be associated with the impact of a body with the composition of ordinary chondrite. Similarly, they found a lack of correlation of Ir with other elements (e.g., Cs, Al, Cu, and V) that might provide a signature of volcanically derived material. Therefore, the authors considered a volcanic source for the enrichment unlikely.

We extend the studies of Olsen et al. [4,5] by examining the concentrations of PGEs and other elements in sediments of the Fundy basin that correlate stratigraphically with those of the Newark basin.

2. Study area and prior work

The Fundy basin (Fig. 1), comprising the contiguous Minas, Fundy, and Chignecto structural sub-basins, formed by left-oblique slip on the Minas fault zone, a reactivated transform that superimposed the Meguma and Avalonian terranes during the late Paleozoic [8]. The basin was a terrestrial rift valley that filled with mostly red-bed sediments and tholeiitic basalts during Middle Triassic to Early Jurassic time. The Blomidon Formation of the Fundy Group comprises 200 to 300+ m of cyclically interbedded sandstone and mudstone interpreted as sediment that accumulated in playa, sandflat, minor lacustrine, eolian, and fluvial environments [9]. A semi-arid to arid climate prevailed in the Fundy basin during the Late Triassic [9,10], and average sediment accumulation rates were possibly as low as ~0.02 mm/year. The formation is overlain by the North Mountain Basalt, dated at 201.7 ± 1.3 Ma [11].

In the Minas sub-basin, a palynological transition interpreted as the TJB occurs in strata of the uppermost Blomidon Formation [12], although correlation of this horizon to European TJB sections remains problematic (see review in [2]). The pollen assemblage in the lacustrine and sheetflood mudstones and siltstones in the upper few meters of the Blomidon Formation exhibits a transition from dominantly *Corollina torosa* and *Patinasporites densus* to mainly *Corollina* spp. (*C. meyeriana*, *C. torosa*, *C. simplex*, *C. murphyea* [12]). This palynological turnover has been documented at only one location in the Fundy basin; on the west side of Partridge Island, near the town of Parrsboro, Nova Scotia, the transition occurs between 30 and 40 cm below the North Mountain Basalt (Figs. 1 and 2) [12]. However, no “fern spike,” as described in the Newark basin [5], has been found in the Partridge Island section.

Orth et al. [13] initially reported slightly elevated Ir levels (up to 0.15 ng/g) in the uppermost Blomidon

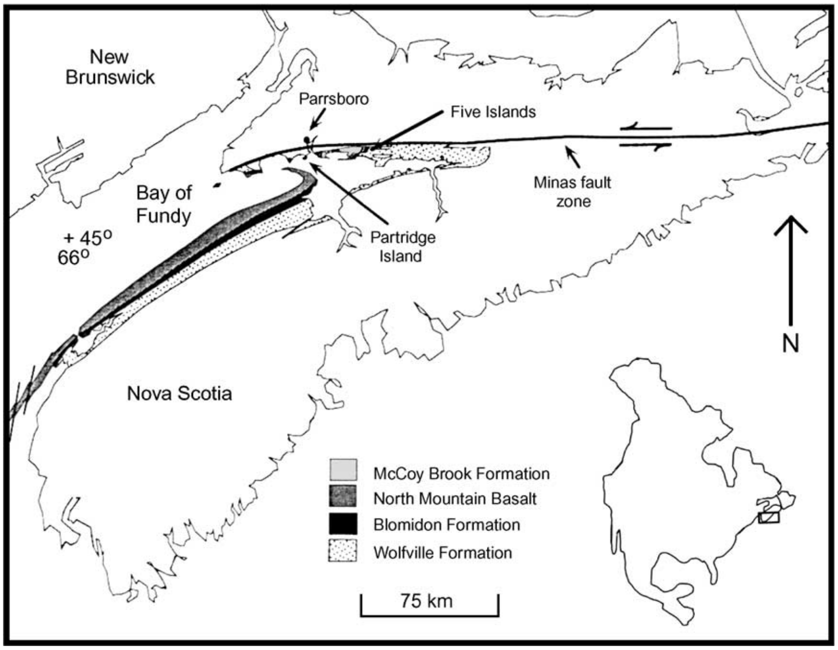

Fig. 1. Location and geologic map of the study area in the Fundy basin. Samples analyzed in this study were collected from Partridge Island, near Parrsboro, Nova Scotia (adapted from [12]). MSB = Minas sub-basin; CSB = Chignecto sub-basin; FSB = Fundy sub-basin.

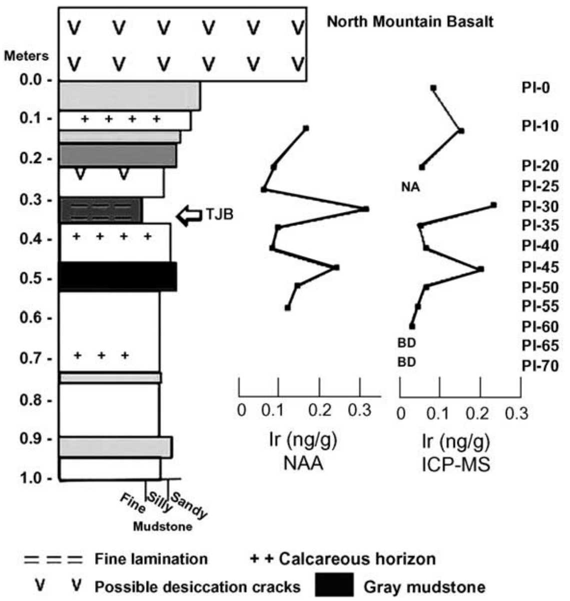

Fig. 2. Lithostratigraphy of the uppermost meter of the Blomidon Formation and Ir concentrations determined by NAA and ICP-MS analyses. Sample identification numbers demarcate the depth (in centimeters) below the contact with the North Mountain Basalt of the top of the 5-cm sample interval. Ir is plotted as the mid-point of the sample interval. TJB = position of Triassic–Jurassic boundary as determined by palynology [12]. NA = sample not analyzed; BD = concentration below detection limit.

Formation of the Fundy basin. Specifically, they found the peak concentration in a sample from 30 cm below the North Mountain Basalt collected from the south side of the basin (location reported in [14]). Mossman et al. [14] later reported a maximum iridium level of about 0.20 ng/g in a sample collected 2 m below the North Mountain Basalt on the north side of the basin at Five Islands (Fig. 1). These earlier studies lacked close sampling resolution, however, and no previous studies have examined the strata in the boundary section at Partridge Island.

3. Lithostratigraphy

The uppermost Blomidon Formation at Partridge Island consists of interbedded red and grey mudstones (Fig. 2). The red mudstones form massive-appearing beds 2–15 cm thick and generally consist of an assemblage of hematite-stained clays, silt to sand-size detrital grains, a minor component of discrete organic debris, and micritic to sparry calcite with a patchy distribution. The detrital grain fraction comprises mostly quartz, with lesser amounts of orthoclase and micas, and minor plagioclase and metamorphic rock fragments. Calcite cement is abundant at several horizons, resulting in nodular weathering of the mudstone. Gray mudstones vary in character from uniformly light greenish-gray beds 2–5 cm in thickness to fine (mm-scale) dark gray to black laminae interlayered with light gray to red mudstone laminae. Petrographic examination confirms that the dark laminae are organic-rich. The uniformly gray mudstones generally contain a higher component of sand-size grains (up to 50%), comprising mostly quartz, igneous (granitic) rock fragments, and metamorphic rock fragments. 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 in most of the section or between the red and gray mudstone beds. The most notable exception is an abundance of chlorite in a greenish-gray mudstone 20 cm below the contact with the North Mountain Basalt.

4. Sampling and analytical methods

The boundary section at Partridge Island is a cliff face partially covered by colluvium. The uppermost 1.0 m of the Blomidon Formation was exposed in a trench and sampled at 5 cm intervals. Each sample represents an interval of 5 cm of strata below the sample point designated by the sample identification number, as measured in centimeters below the contact with the basalt. The Triassic–Jurassic boundary, identified at this location by palynology [12] was encompassed by the interval of sample PI-30 (i.e., 30–35 cm below the basalt; Fig. 2).

One 20 g split of the sample suite was used for neutron activation analysis (NAA) of Ir and other selected elements. A split of ~3 g of rock was baked in quartz-glass crucibles at 450 °C to drive off volatiles and then powdered in a hi-purity alumina mortar. Sample splits of ~100 mg of powder were sealed in quartz-glass vials and were 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, Hf, Ta, and Th concentrations. Iridium was then chemically purified using a method similar to that described by Schellenberg et al. [15] prior to counting. Multiple splits of rock powders were used as standards. An internal powder of Allende meteorite was used for Ir and USGS standard rocks BHVO-1 (basalt) and G-2 (granite) were used for the other elements. Typical 1-sigma counting errors for the

NAA data are <10 relative percent, except for Ni which can be as high as 30%.

A second 20 g sample split was analyzed by nickel-sulfide fusion assay technique with ICP-MS measurement to determine the concentrations of five platinum group elements (Ir, Pt, Pd, Rh, Ru) plus Au. These analyses were conducted by Geoscience Laboratories (Sudbury, Ontario), a division of the Ontario Geological Survey. Samples were fused with Ni and S to produce a nickel sulfide button that subsequently was dissolved. The metals were then co-precipitated with Te and re-dissolved for analysis by a Perkins-Elmer ELAN 6100DRC inductively coupled plasma mass spectrometer. The detection limits, calibrated to internal standards, are as follows: Ir = 0.04 ng/g; Au = 0.71 ng/g; Pd = 0.11 ng/g; Pt = 0.14 ng/g; Rh = 0.08 ng/g; and Ru = 0.13 ng/g. Replicate analyses indicate an accuracy of measurement to ± 0.02 ng/g.

Major element analyses (Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, and Si as oxides) were conducted by X-ray fluorescence (XRF) of a separate sample split fused with a borate flux. These analyses were conducted by Geoscience Laboratories using a Rigaku RIX-3000 wavelength dispersive X-ray fluoresecence spectrometer. The clay mineralogy (reported above) was determined by X-ray diffraction on oriented mounts of <2 μm separates prepared from a fourth split of the sample suite using a Scintag X1 powder diffractometer at Bloomsburg University of Pennsylvania. Standard (30 μm) thin sections were prepared from the samples for petrographic analysis.

5. Results

Results from NAA and ICP-MS exhibit good agreement in displaying a pattern of Ir enrichment at multiple horizons within the section (Fig. 2; Tables 1 and 2); both methods identify the peak Ir concentration of 0.31 ng/g (NAA) and 0.23 ng/g (ICP-MS) in sample PI-30, which encompasses the TJB. Secondary peaks of Ir enrichment are identified in samples PI-45 (0.24 ng/g by NAA, 0.20 ng/g by ICP-MS) and PI-10 (0.17 ng/g by NAA, 0.15 ng/g by ICP-MS). The lowest Ir concentration measured by NAA is 0.07 ng/g in sample PI-25; this sample was not analyzed by ICP-MS. Samples PI-60 and PI-70 yielded Ir concentrations below the detection limit (for ICP-MS) of 0.04 ng/g. These samples were not analyzed by NAA so the background Ir level for the section is unknown, but presumed lower than 0.04 ng/g.

Among other elements analyzed by ICP-MS, Au displays the strongest correlation with Ir (Fig. 3; $R = 0.78$, $p \le 0.01$); peak concentrations of 7.57 and 7.53 ng/g coincide with peak Ir values in samples PI-30 and PI-45. Concentrations of Pt also correlate with Ir, but not as strongly as for Au ($R = 0.59$, $p = 0.04$). Pd also appears to correlate weakly with Ir, but not at a statistically significant level ($R = 0.48$, $p > 0.1$). Concentrations of Rh and Ru were below the detection limits for this method in most samples. Notably, the peak concentrations of Pd, Pt and Ru occur in sample PI-0, representing the 5-cm interval immediately below the

Table 2
Results of analysis of Partridge Island Blomidon samples by ICP-MS (all results in ng/g), CI—chondrite data for reference [19]

ID#	Au	Ir	Pd	Pt	Rh	Ru
PI-0	4.20	0.09	4.51	1.57	<0.08	0.14
PI-10	5.20	0.15	3.81	1.43	0.09	0.13
PI-20	1.82	0.05	1.52	0.83	<0.08	<0.13
PI-30	7.57	0.23	2.56	1.16	<0.08	<0.13
PI-35	1.20	0.05	0.71	0.33	<0.08	<0.13
PI-40	1.81	0.06	0.79	0.42	<0.08	<0.13
PI-45	7.53	0.20	2.1	0.75	<0.08	<0.13
PI-50	5.69	0.06	1.43	0.89	0.09	<0.13
PI-55	2.40	0.05	0.59	0.5	<0.08	<0.13
PI-60	3.80	0.04	0.79	0.57	<0.08	<0.13
PI-65	3.10	<0.04	0.98	0.43	<0.08	0.13
PI-70	3.69	<0.04	2.08	0.37	<0.08	<0.13
CI	145	465	560	1,000	140	710

Table 1
Results of analysis of Partridge Island Blomidon samples by NAA

ID#	Sc (μg/g)	Cr (μg/g)	Fe (mg/g)	Co (μg/g)	Ni (μg/g)	Zn (μg/g)	Cs (μg/g)	Ce (μg/g)	Eu (μg/g)	Hf (μg/g)	Ta (μg/g)	Th (μg/g)	Ir (ng/g)
PI-10	8.7	48	66	39	40	239	2.0	32	0.92	2.7	0.6	6.3	0.17
PI-20	11.2	59	26	12	44	256	6.6	127	1.71	7.3	1.1	10.0	0.09
PI-25	14.9	73	48	17	45	157	9.8	72	1.35	5.3	1.2	10.5	0.07
PI-30	15.2	82	44	17	36	269	10.4	106	1.72	5.6	1.2	11.7	0.31
PI-35	8.5	58	25	7	23	53	4.5	69	1.36	7.5	0.9	8.7	0.09
PI-40	9.6	58	28	9	25	118	5.2	61	1.14	5.7	1.0	8.3	0.08
PI-45	12.8	77	32	12	42	471	8.5	77	1.34	6.5	1.1	11.4	0.24
PI-50	13.2	72	36	14	48	108	8.9	83	1.55	6.4	1.1	10.8	0.14
PI-55	12.3	67	37	13	43	68	8.5	85	1.43	6.9	1.2	11.2	0.12

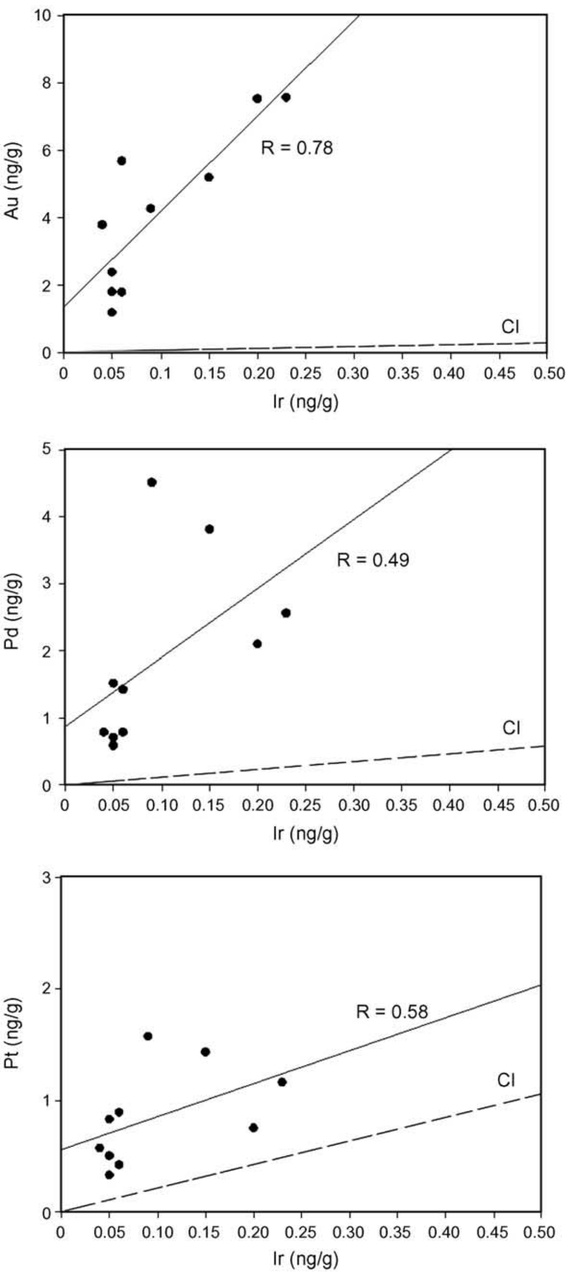

Fig. 3. Concentrations of Pt, Au and Pd plotted against Ir concentrations as determined by ICP-MS analysis plotted with line of least-squares regression. Ratio for CI chondrite from [18] plotted as a dashed line for comparison. Actual CI concentrations plot off scale.

basalt (this sample was not analyzed by NAA). Among transition group elements analyzed by NAA, Zn, Co, Cr, and Fe appear to correlate weakly with Ir concentration (Fig. 4), with Zn correlating most strongly ($R = 0.64$, $p = 0.06$). None of these correlations are statistically significant at the 95% confidence level. All other transition element and REE abundances display a lack of correlation with Ir concentration. Similarly, there is no apparent correlation between major element abundances, as determined by XRF, and Ir (Table 3).

6. Discussion

We report here the identification of multiple horizons in the Partridge Island section in which Ir and other siderophile elements are measurably enriched. We resist over-interpretation of these data pending re-sampling and analysis of this stratigraphic section at higher resolution. Nonetheless, we note several trends in the distributions of the elements analyzed in this study. First and foremost is that the peak abundance of Ir occurs in sample PI-30, which encompasses the interval from 30 to 35 cm below the basalt. This is the stratigraphic level identified as the horizon of palynological turnover that has been interpreted as the TJB [12]. The magnitude of this enrichment is similar to that observed by Olsen et al. [4,5] at the palynological boundary in the Newark basin so it is reasonable to conclude that the Ir enrichment is a correlative phenomenon of at least regional extent. We note that the multiple enrichment intervals at Partridge Island occur in mudstones that are gray to laminated; i.e., Ir enrichment was not detected in the red mudstones, whereas in the Newark basin Ir enrichment appears independent of lithology [5]. Consequently, we consider here the possibility that Ir enrichment at multiple levels in the gray mudstones is associated with diagenetic remobilization and redox boundary conditions. Studies of PGEs in marine sediments have noted the mobility of Ir under reducing conditions [16,17].

In contrast to the results from the Newark basin [5], our results indicate covariance of Ir and some PGEs (Pd and Pt) plus Au (Fig. 3), as noted above. Caution is probably advised in interpreting the ratios of these elements when they occur at such low concentrations; nonetheless, we note that the ratios of Pd, Pt and Au to Ir exceed ratios for ordinary chondrites [18,19], typically by an order of magnitude for Au and Pd, and more closely resemble ratios characteristic of basalts or hydrothermal fluids [20]. We note also that the overlying North Mountain Basalt is locally enriched in Ir and other PGEs [21]. Greenough and Fryer [21] report PGE data on a suite of 36 samples from this flood basalt sequence, demonstrating a wide range of compositions that reflect differentiaion from large flow units. Orthopyroxene (opx) basalts at the base of the formation average 0.45 ng/g and one sample is as high as 1.00 ng/g. Some associated rhyolites also contain up to 1.00 ng/g Ir. Other PGEs are also abundant in these

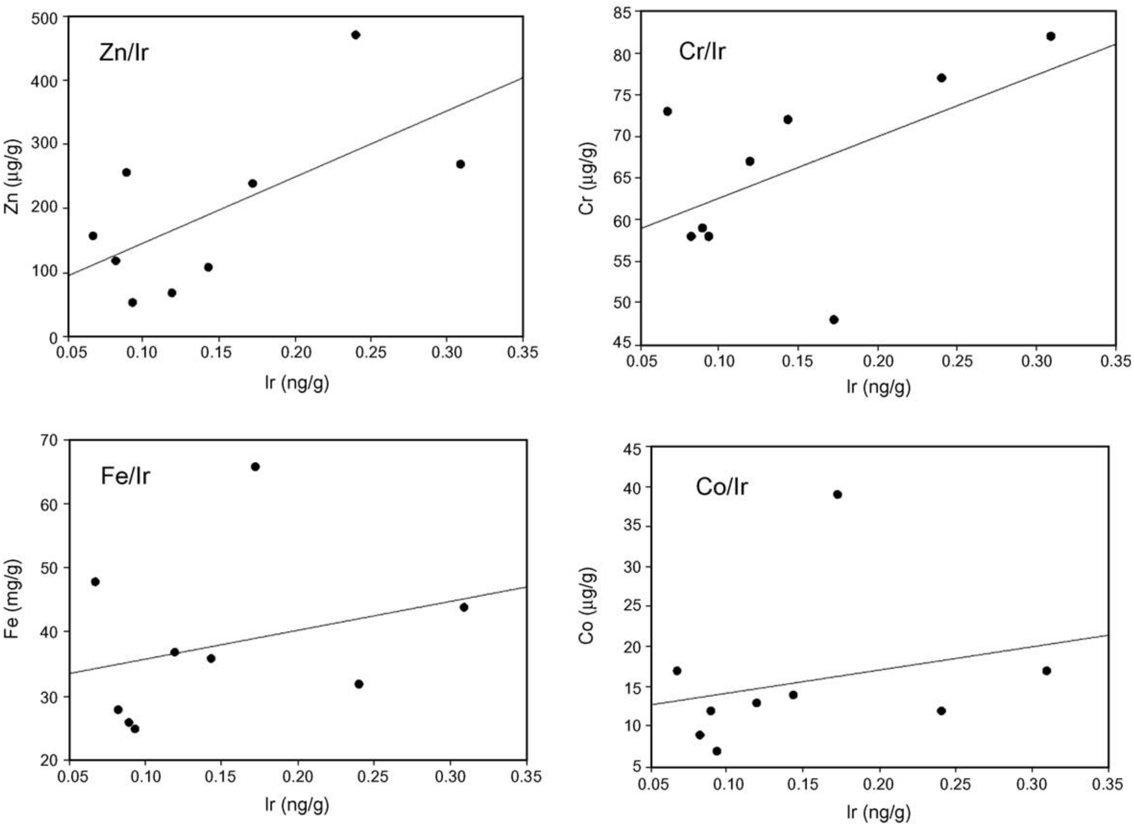

Fig. 4. Concentrations of Zn, Cr, Fe, and Co plotted against Ir concentrations as determined by NAA. Line is least squares linear regression.

rocks. For example, average concentrations for Au, Pt, Pd, Rh, and Ru from five specimens of opx basalts were 1.8, 5.6, 8.1, 0.47, and 0.46 ng/g, respectively. The opx basalts pinch out eastward several kilometers to the west of the study area, however, and thus do not occur above the TJB in the Partridge Island section [21]. Vesicular basalts higher in the formation have average Ir values of 0.09 ng/g. In both opx and vesicular basalts Au, Pt, and Pd are generally enriched relative to Ir [21], yet the North Mountain Basalt also contains Rh and Ru in abundances approximately equal to Ir. The Blomidon samples that contain peak Ir concentrations lack measurable enrichment in Rh and Ru and therefore do not display PGE ratios typical of either basalt or ordinary chondrite. Our petrographic analyses show no clear evidence of detritus from either basaltic eruptions or impact ejecta in these sediments. Clearly, if the Ir in these samples is derived from some impact

Table 3
Results of major element analysis of Partridge Island Blomidon samples by XRF (reported as weight-percent oxides)

ID#	SiO_2	TiO_2	Al_2O_3	MnO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total
PI-0	32.07	0.51	12.52	0.24	8.63	16.68	9.66	0.09	1.45	0.09	17.09	99.12
PI-10	42.93	0.21	5.05	0.37	5.59	5.43	20.76	0.08	0.34	0.06	19.07	99.91
PI-20	68.16	0.76	11.50	0.06	4.88	5.59	1.26	0.26	3.23	0.11	5.33	101.14
PI-30	54.68	0.75	14.37	0.11	5.85	7.84	3.94	0.27	3.43	0.11	10.08	101.45
PI-35	49.39	0.60	9.60	0.27	4.12	4.95	13.51	0.17	2.71	0.09	14.84	100.25
PI-40	54.09	0.62	9.82	0.22	3.86	4.42	11.66	0.11	2.93	0.09	12.63	100.46
PI-45	48.80	0.69	11.86	0.22	3.94	6.42	10.78	0.47	2.96	0.10	14.06	100.32
PI-50	64.08	0.79	12.68	0.08	4.32	7.18	1.53	0.19	3.63	0.12	6.56	101.16
PI-55	62.29	0.77	13.16	0.09	5.69	6.85	1.75	0.18	3.89	0.13	6.41	101.2
PI-60	62.98	0.83	14.88	0.06	4.31	6.64	0.71	0.3	4.41	0.12	5.99	101.22
PI-65	69.62	0.79	12.68	0.06	4.16	4.90	0.36	0.29	4.10	0.10	4.30	101.35
PI-70	64.68	0.80	13.37	0.07	5.23	5.69	0.55	0.24	4.28	0.11	5.10	100.11

source, either the PGEs have been strongly fractionated, or the bulk of the PGEs other than Ir must be derived from terrestrial sources.

Previous attempts to identify evidence of bolide impact at the TJB have yielded results considered equivocal at best. Mossman et al. [14] examined grains with lamellar features from strata in the upper part of the Blomidon Formation with TEM, but these authors failed to detect any evidence of a shock metamorphism origin for the lamellae. Petrographic analyses of the samples collected for this study have not yet yielded any evidence of materials with a possible impact origin, nor have there have been any verifiable reports of shocked mineral grains, impact glass (microtektites, tektites), micro-spherules, Ni-rich spinels, micro-diamonds or soot at or near the TJB at any other location globally. Earlier reports of quartz grains containing multiple planar deformation features at the TJB sections at Kendelbach, Austria [22] were based on inadequate petrographic techniques and have been discounted [23]. Shocked quartz grains have been reported from multiple stratigraphic intervals below the TJB in a section near Corfino, northern Italy [24], but this report has not been corroborated [23].

New data demonstrate the initiation of the long-term eruptions in the Central Atlantic Magmatic Province (CAMP) in some parts of the province prior to the TJB [25]. Therefore, the occurrence of an Ir enrichment zone below the lowest CAMP basalts in the Newark basins does not exclude a volcanic source of siderophile enrichment. Outgassing of mantle derived magmas has been suggested previously for Ir anomalies at some geological boundaries [26], although there are no specific data to support this hypothesis yet. Olmez et al. [27], for example, have estimated that approximately 0.3% of the Ir in magma erupted from Kilauea enters the atmosphere. Hypothetically, the eruption of a sufficient volume of magma containing elevated levels of Ir would have produced a measurable anomaly in local sedimentary deposits. Conversely, the inter-element ratios reported here do not match those of volcanic exhalations, nor does the Blomidon Formation section examined in this study contain a smectite-rich clay layer, as does the Jacksonwald syncline section [4,5], that might be associated with volcanic activity. At present, there are insufficient data on both the geographic extent and level of the Ir enrichment at the TJB and on the composition and precise timing of the eruptions of the CAMP basalts to resolve this issue. Thus, at this time, both extraterrestrial and mantle-derived sources for the elevated iridium levels at the system boundary remain viable hypotheses.

7. Conclusion

There is enrichment of some PGEs (including Ir) and transition group elements in strata that occur at, and in close stratigraphic proximity to, the horizon of palynological turnover that is interpreted as the TJB in the Fundy basin. This enrichment correlates with other reports of elevated Ir at other sites in the Fundy basin and the Newark basin, indicating that this is a regional phenomenon. At this time, it is unclear what the source of this enrichment is and to what extent these elements have been subject to remobilization. We plan additional sampling and analyses of the Partridge Island section at a greater (i.e., 1 cm) resolution in the hope that new data will allow us to discriminate among the possible sources for the Ir enrichment.

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