

Discovery of a meteoritic ejecta layer containing unmelted impactor fragments at the base of Paleocene lavas, Isle of Skye, Scotland

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ABSTRACT

Evidence for meteorite impacts in the geological record may include the presence of shocked minerals, spherule layers, and geochemical anomalies. However, it is highly unusual to find unmelted crystals from the actual impactor within an ejecta layer. Here we detail the first recorded occurrence of vanadium-rich osbornite (TiVN) on Earth, from two sites on Skye, northwest Scotland, which are interpreted as part of a meteoritic ejecta layer. TiVN has only previously been reported as dust from comet Wild 2, but on Skye it has been identified as an unmelted phase. Both ejecta layer sites also contain niobium-rich osbornite (TiNbN), which has not previously been reported. An extraterrestrial origin for these deposits is strongly supported by the presence of reidite (a high-pressure zircon polymorph), which is only found naturally at sites of meteorite impact. Barringerite [(Fe,Ni)₂P], baddeleyite (ZrO₂), alabandite (MnS), and carbon-bearing native iron spherules, together with planar deformation features and diaplectic glass in quartz, further support this thesis. We demonstrate through field relationships and Ar-Ar dating that the meteorite strike occurred during the mid-Paleocene. This is the first recorded mid-Paleocene impact event in the region and is coincident with the onset of magmatism in the British Palaeogene Igneous Province (BPIP). The Skye ejecta layer deposits provoke important questions regarding their lateral extent at the base of the BPIP and the possibility of their presence elsewhere beneath the much larger North Atlantic Igneous Province.

BACKGROUND

Meteorite impact deposits are found throughout the geological record. However, in this paper we detail the youngest recorded UK meteorite impact event, located beneath mid-Paleocene lavas (Fig. 1A) at 2 sites 7 km apart on what is now the Isle of Skye, northwest Scotland (Fig. 1B). The only other known meteoritic ejecta deposit in Scotland is much older (1177 ± 5 Ma) than the Skye deposits and occurs within Precambrian rocks on the Scottish mainland (Parnell et al., 2011; Reddy et al., 2015).

We present compelling mineralogical and textural evidence within the Skye deposits for impact-derived shock metamorphism at pressures ≥30 GPa. Within the deposits at both sites, unmelted vanadium-rich osbornite (TiVN) and niobium-rich osbornite (TiNbN) are preserved as part of the actual impactor. Recognition of actual unmelted impactor mineralogy has previously only been from the Chicxulub crater on the Yucatan Peninsula (Kyte, 1998).

The methodology employed during our study comprises field observations, petrography, electron microprobe analysis, Raman microscopy, U-Pb and Ar-Ar radiometric dating, and

extensive comparative geochemistry (see the GSA Data Repository¹).

FIELD RELATIONS AND CHEMISTRY OF METEORITIC EJECTA LAYER DEPOSITS AT SITES 1 AND 2

The Isle of Skye forms part of the British Palaeogene Igneous Province (BPIP), a volcanic region that extends from the Inner Hebrides of Scotland to Northern Ireland. Igneous activity on Skye spanned ca. 61–54.5 Ma (Bell and Williamson, 2002). The BPIP forms part of the North Atlantic Igneous Province, a 1.3 × 10⁶ km² area (Eldholm and Grue, 1994; Fig. 1A).

Site 1 is located at An Carnach on the Strathaird Peninsula (Figs. 1B, 2A, and 2B), where a 0.9-m-thick meteoritic ejecta layer overlies Middle Jurassic sedimentary rocks (Drake

¹GSA Data Repository item 2018039, detailed methodologies, geochronology and comparative geochemistry of osbornite, barringerite, reidite, alabandite, native iron, and additional shocked images, is available online at <http://www.geosociety.org/datarepository/2018/> or on request from editing@geosociety.org.

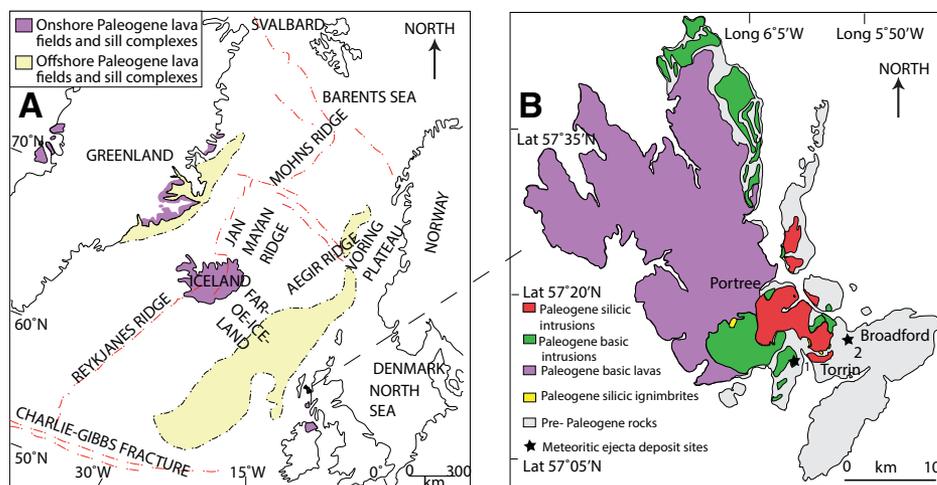


Figure 1. A: North Atlantic Igneous Province (modified from Saunders et al., 1997). B: Simplified geological map of the Isle of Skye, Scotland, showing the location of meteoritic ejecta layer deposits at sites 1 and 2.

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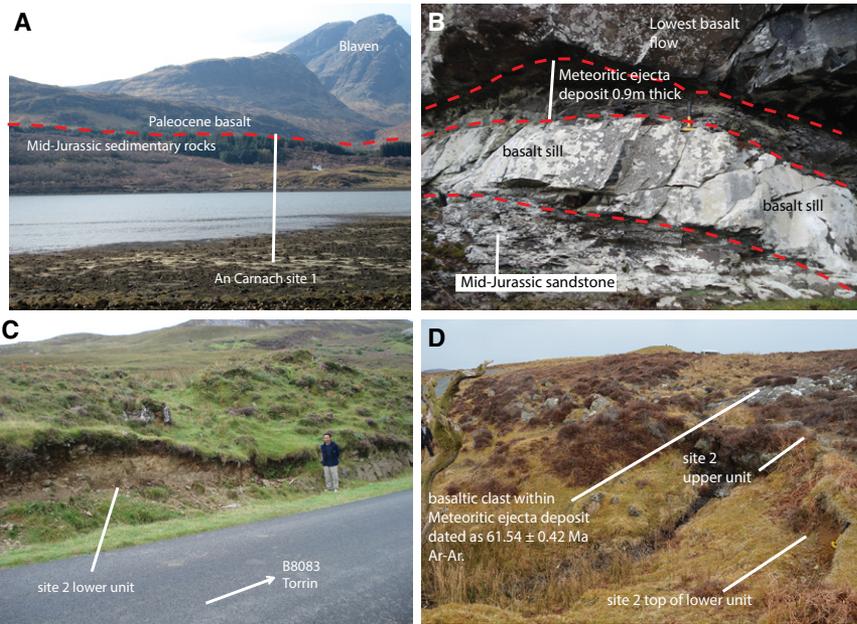


Figure 2. Field relationships at both meteoritic ejecta layer sites. **A:** Location of site 1 (grid reference NG 55371 21112 at the base of An Carnach plateau lavas. **B:** Site 1 deposit at the base of the plateau lavas (NG 55371 21112). Basaltic sill has chilled margins and intruded at the earlier contact between meteoritic ejecta layer deposit and Middle Jurassic Valtos sandstone. **C:** Location of site 2 lower unit of layer (NG 62626 21860). This unit crops out on top of Cambrian–Ordovician dolostone 50 m north-northeast (NG 62730 21955). **D:** Site 2 lower unit (NG 62627 21858) grading into an upper unit (NG 62627 21890) that contains a basaltic clast dated as 61.54 ± 0.41 Ma (Data Repository; see footnote 1). Hammer shaft in B and D is 35 cm length. Field of view in A is 1.5 km across skyline.

and Beard, 2012) and underlies 70 m of mid-Paleocene basaltic lavas (Fig. 2A; Fig. DR2 in the Data Repository). The meteoritic ejecta layer comprises ≥ 95 vol% matrix, with a composition of 47 wt% SiO_2 and high Al_2O_3 and FeO, and resembles volcanic ash altered to potassium-rich clay. It has a matrix fabric similar to that of a welded ignimbrite deposited from a low-concentration pyroclastic density current.

Site 2 is located on route B8083 (Figs. 1B, 2C, and 2D), 1.5 km south-southwest of Broadford. Here the meteoritic ejecta layer is 2.1 m thick, comprising a crudely stratified, 0.9-m-thick lower pumiceous-like subunit reminiscent of an unwelded terrestrial ignimbrite (Figs. 2C, 2D; Fig. DR2). This lower unit crops out unconformably on Cambrian–Ordovician dolostone and varies laterally in thickness from 0.25 to 0.90 m. This lower unit grades upward to a 1.2-m-thick, coarser upper subunit that is largely clast supported with variable amounts of matrix. The upper subunit contains heterolithic components including sporadic outsized blocks of basalt as large as to 1.15×0.7 m (Fig. 2D). One basaltic block has been dated as 61.54 ± 0.42 Ma using the ^{40}Ar – ^{39}Ar system (Figs. DR1 and DR3; Table DR1).

MINERALOGY OF METEORITIC EJECTA LAYER DEPOSITS AT SITES 1 AND 2

The site 1 layer has a very fine grained matrix comprising quartz, orthoclase, and clay-rich streaked domains, which are deflected around quartz crystals and granitic and basaltic lithic lapilli. Undeformed bubble wall shards are evident in pressure shadows. Common accessory phases are rutile, monazite, and zircon, together with rare chromite. The site 2 lower layer is also fine grained with a matrix of undeformed glass shards, quartz, and K-feldspar. Within the matrix are arkosic sandstone and gneiss lithic lapilli, ≤ 5 cm. The upper unit at site 2 is largely clast supported and contains subrounded lapilli and blocks of quartzite, arkosic sandstone, and basalt.

Reidite is present and occurs sporadically within matrix zircons at both sites (Figs. 3A and 4A; Fig. DR4; Table DR5). Individual zircons frequently contain reidite shock lamellae (Fig. 4A). This study has employed both Raman microscopy and electron microprobe techniques to detect reidite. Our sample bands and peaks accord well with all known natural reidite Raman bands (Fig. DR4; Table DR5). The presence of reidite shock lamellae (Figs. 3A and 4A) in the Skye samples together with the Raman spectra provide compelling evidence of instantaneous shock pressures in excess of ~ 30 GPa (Leroux et al., 1999). Such pressures can only be derived in nature by impact events.

Our paper reports the first terrestrial finding of both TiVN (Figs. 3B and 3C; Table DR3) and a niobium-rich osbornite (TiNbN) (Fig. 3D;

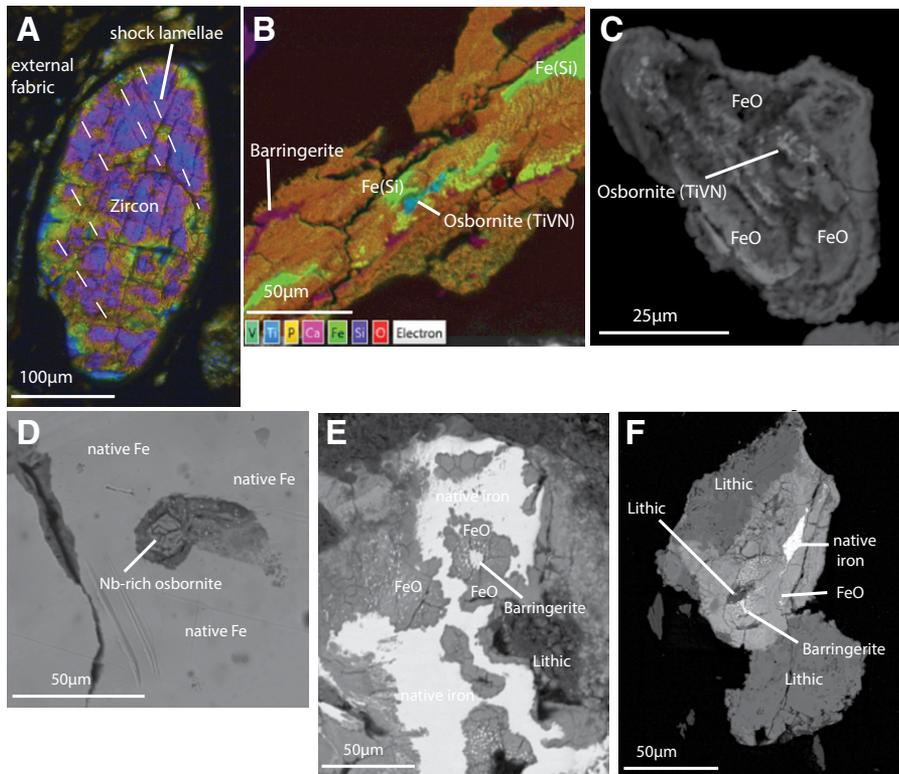


Figure 3. Impact-derived mineralogy. **A:** Zircon from site 1 (grid reference NG 55371 21112) showing top left to bottom right trending reidite-containing shock lamellae. **B:** Electron microprobe X-ray map of an Fe (Si) metal grain from site 2, incorporating TiVN (vanadium-rich osbornite; light blue), barringerite (purple), and native Fe(Si) metal (light green). **C:** TiVN from site 1 mantled by FeO. **D:** Nb-rich osbornite with a hexoctahedral habit surrounded by FeO, likely generated by secondary alteration by fluid. Both the TiVN and FeO are totally encased by native Fe. **E:** Barringerite surrounded by secondary FeO. **F:** Angular native iron surrounded by FeO.

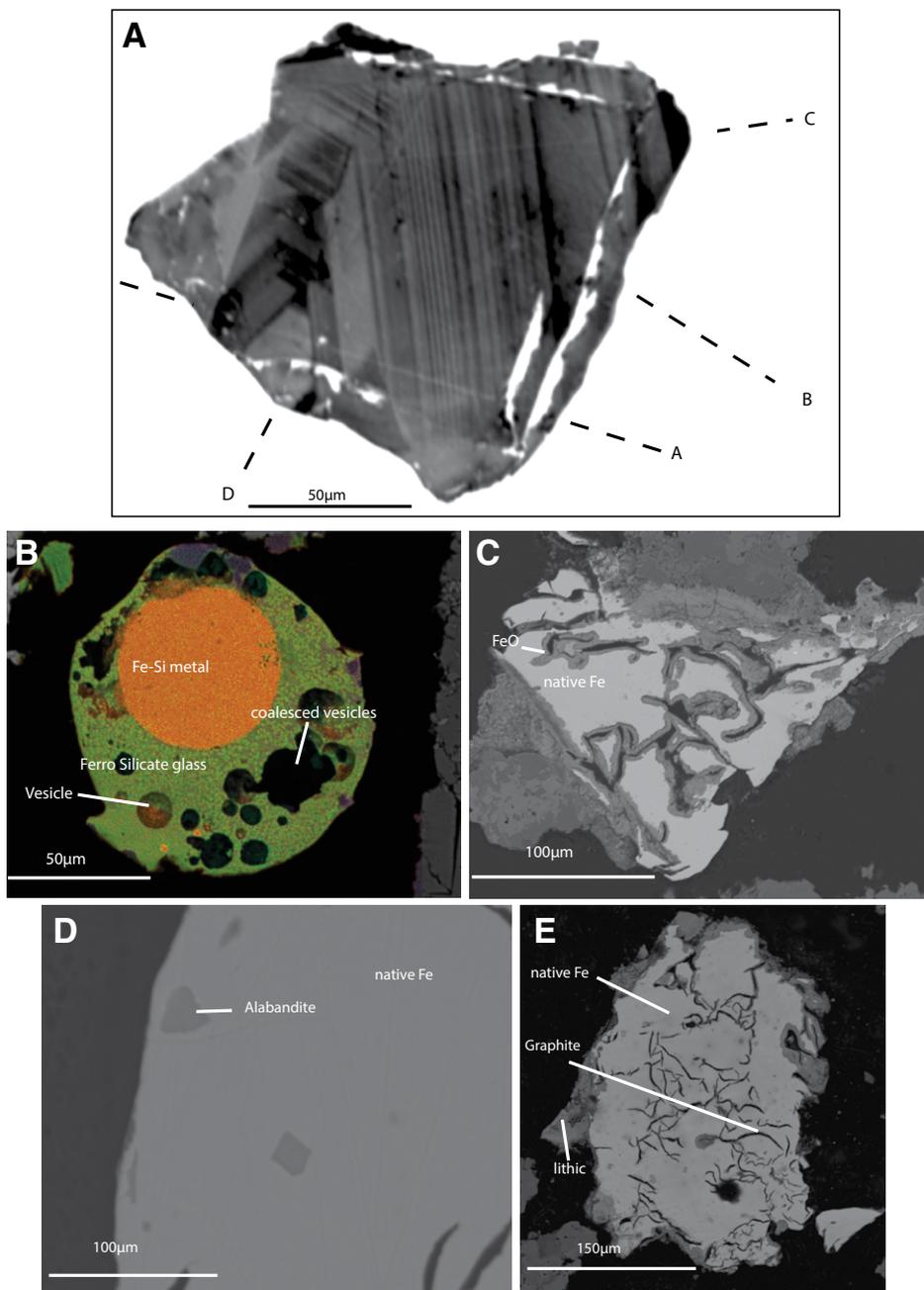


Figure 4. Impact-derived mineralogy. A: Cathodoluminescence image of zircon from site 1. Dashed lines represent crosscutting reidite-containing lamellae. **B:** X-ray elemental distribution map of a ferrospherule from site 2 comprising a central core of highly reduced native Fe(Si) (orange) mantled by a ferrosilicate glass (green). **C:** Vermicular graphite trails that have exsolved out of native iron. **D:** Euhedral to subhedral isometric ferroan alabandite within a native iron fragment from site 1. **E:** Abundant vermicular-like graphite and rare subhedral ferroan alabandite inclusions within a native iron fragment.

Table DR3) phase. Within both Skye meteoritic ejecta layer deposits, grains of TiVN occur sporadically throughout the matrix (Figs. 3B and 3C). These grains are frequently in very close spatial association with barringerite [(Fe,Ni)₂P] (Fig. 3B). At both sites, a hitherto-unrecognized V-Nb-osbornite-type phase occurs as rare, 10–30 µm irregularly fractured inclusions (Fig. 3D; Table DR3) within native-Fe containing trace amounts of Si, Ni, and Cu. The TiNbN

phase is frequently mantled by FeO rims that are encased by native metal domains. This V-Nb-osbornite is remarkably similar in chemistry to TiVN recovered from the NASA Stardust mission to comet 81P/Wild 2 (Chi et al., 2009). At site 2, the V-Nb-osbornite is probably a carbonitride, because it contains 11 wt% carbon.

Pure osbornite (TiN) is an extremely rare mineral that has been found extraterrestrially as comet dust (Chi et al., 2009) or as trace

amounts within carbonado diamonds (Garai et al., 2006). Such diamonds are possibly extraterrestrial in origin. On Earth, only pure TiN has been found. This pure TiN occurs as inclusions within coesite in Tibetan ophiolite (Dobrzhinetskaya et al., 2009) and within coesite-bearing eclogite in the Dabie Mountains, China (Wu et al., 2005). Osbornite in Wild2 comet dust varies from TiN to TiVN (Chi et al., 2009). The presence of TiVN provides unequivocal evidence of extraterrestrial genesis. The coexistence of TiNbN and TiVN within the meteoritic ejecta layer deposits suggests that a solid solution series may exist between the three phases.

Barringerite occurs within native metal fragments at both sites (Figs. 3B, 3E, and 3F; Table DR4); it has been found terrestrially within either natural phosphide or Cu-Ni sulfide deposits (Chen et al., 1984), but neither of these types of deposits is known on Skye. However, barringerite is well known from meteorites (Brandstätter et al., 1991).

Baddeleyite is found in close association with reidite-bearing zircon at both sites. Baddeleyite, while present in terrestrial intrusions, has also been found in achondrites and lunar meteorites (Heaman and LeCheminant, 1993).

We note the sporadic presence of alabandite within the matrix (Fig. 4D; Table DR6) at both sites. Alabandite, while common in terrestrial metallic sulfide deposits, has been also been used to determine thermometry of enstatite chondrites (Zhang and Sears, 1996).

The zircon populations within the matrix at both sites have been dated using the U-Pb system and show a wide range in ages, from 3227 to 249 Ma (Figs. DR1 and DR5; Tables DR2 and DR7), dominated by 2 peaks ca. 2800–2600 Ma and 1800–1600 Ma (Fig. DR1). We interpret these peak zircon ages as being derived from Archean and Proterozoic rocks that were incorporated by meteorite impact. These rocks are represented by basement gneiss, present as sporadic lapilli at site 2, and arkosic sandstone lapilli, present at both sites. It is important that these U-Pb ages are highly unlikely to be reset by shock damage or shock transformation to reidite (Timms et al., 2015).

Rare microscopic spherules (~20 µm) of native iron at both Skye sites have oxidized FeO margins and vesiculated silicate glass rims (Fig. 4B; Table DR8). X-ray element maps indicate that iron spherules at site 2 are larger, ≤40 µm in diameter, vesiculated, with native Fe(Si) cores and ferrosilicate glass mantles (Figs. 4B–4D). Native iron is not unique to meteorite impact and occurs rarely on Earth. The shape, texture, and chemistry of Skye spherules strongly suggest that crystallization was rapid, in conditions of very low oxygen fugacity (Grebennikov, 2011).

At both Skye sites, matrix quartz occasionally displays planar deformation features (Fig. DR6a).

DISCUSSION AND CONCLUSIONS

The exotic mineralogy and whole-rock bulk matrix chemistry at both meteoritic ejecta layer sites on Skye are extremely similar. Both sites contain reidite and V-rich osbornite that provide compelling evidence of impact derivation. The barringerite and native iron spherules support this conclusion. The site 1 meteoritic ejecta layer was deposited unconformably on Middle Jurassic sedimentary rocks and is conformable with the base of overlying mid-Paleocene lavas, and the site 2 meteoritic ejecta layer was deposited unconformably on Cambrian–Ordovician dolostone. At both sites generation likely occurred by progressive aggradation (Branney and Kokelaar, 2002) within a fully dilute, low-concentration turbulent flow. The increased sizes of components in the upper parts at site 2 suggest that current flow dynamics changed to reflect an increase in energy at the source.

Field, chemical, and mineralogical evidence suggest that impact occurred very early in Skye's volcanic evolution; this would account for a lack of mid-Paleocene zircons within either deposit.

The basaltic block at site 2 has been dated as 61.54 ± 0.42 Ma (Fig. DR3; Table DR1) and, because it is incorporated within the meteoritic ejecta layer deposit, was in existence before the meteorite strike. Therefore, some basaltic magmatism must have predated impact.

We have attempted to determine the impact age. The event must have taken place prior to eruption of the earliest lavas above the meteoritic ejecta layer at site 1. These lavas belong to the Skye Main Lava Series, which are 60.00 ± 0.23 Ma (Chambers et al., 2005); therefore, impact cannot have occurred after this date. The impact cannot be earlier than the age of the basaltic block (61.54 ± 0.42 Ma) within the upper unit at site 2 (Fig. DR3; Table DR1).

The meteoritic ejecta layer deposits at both sites suggest that the impactor was very reduced, with mineralogy representative of that found in enstatite chondrites (Jacquet et al., 2015). It is tempting to speculate on the extent of the Skye ejecta layer and location of the possible source crater. Because zircon population ages within the meteoritic ejecta layer deposits at both sites cluster around the Archean and Proterozoic (Fig. DR1), host gneiss and arkosic sandstone were necessarily available locally. The pre-Paleocene land surface in the local vicinity probably comprised both these lithologies (Beard and Drake, 2007). Thus, zircon incorporation as a result of impact could have been at or near the paleoland surface. Conversely, these zircon ages accord well with those in Scandinavia, Greenland, and Canada, so the crater could have been from several places in the Northern Hemisphere; there is no indication that it was confined to Scotland. Determining the spatial association of the Skye deposits with the source crater is further hampered by recent glaciations and by

the depositional mechanism of the meteoritic ejecta layer, which was likely progressive aggradation (Branney and Brown, 2011). A current produced by such a mechanism would not yield a temporal record of the full impact event at any given locality, and thus the spatial determination of the Skye deposits in relation to any source crater would seem highly problematic.

The age of the Skye meteoritic ejecta layer deposits and their presence at the base of mid-Paleocene lavas provokes important questions regarding the relationship between impact and early BPIP volcanism. Did the impact contribute to flood basalt volcanism, and does the ejecta layer extend further throughout the BPIP, and possibly the wider North Atlantic Igneous Province?

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REFERENCES CITED

- Beard, A.D., and Drake, S.M., 2007, A melilite-bearing high-temperature calcic skarn, Camasunary Bay, Isle of Skye: *Scottish Journal of Geology*, v. 43, p. 57–67, <https://doi.org/10.1144/sjg43010057>.
- Bell, B.R., and Williams, I.T., 2002, Tertiary igneous activity, in Trewin, N.H., ed., *The geology of Scotland* (fourth edition): London, Geological Society of London, p. 371–407.
- Brandstätter, F., Koeberl, C., and Kurat, N., 1991, The discovery of iron barringerite in lunar meteorite Y-793274: *Geochimica et Cosmochimica Acta*, v. 55, p. 1173–1174, [https://doi.org/10.1016/0016-7037\(91\)90170-A](https://doi.org/10.1016/0016-7037(91)90170-A).
- Branney, M.J., and Brown, R.J., 2011, Impactoclastic density current emplacement of terrestrial meteorite-impact ejecta and the formation of dust pellets and accretionary lapilli: Evidence from Stac Fada, Scotland: *Journal of Geology*, v. 119, p. 275–292, <https://doi.org/10.1086/659147>.
- Branney, M.J., and Kokelaar, P., 2002, Pyroclastic density currents and the sedimentation of ignimbrites: *Geological Society of London Memoir* 27, 143 p., <https://doi.org/10.1144/GSL.MEM.2003.027.01.10>.
- Chambers, L.M., Pringle, M.S., and Parish, R.R., 2005, Rapid formation of the small isles Tertiary centre constrained by precise $^{40}\text{Ar}/^{39}\text{Ar}$ and U–Pb ages: *Lithos*, v. 79, p. 367–384, <https://doi.org/10.1016/j.lithos.2004.09.008>.
- Chen, K., Jin, Z., and Peng, Z., 1984, The discovery of iron barringerite (Fe,Ni 2P) in China: *Mineral Abstracts*, v. 35, p. 1871.
- Chi, M., Ishii, H.A., Simon, S.B., Bradley, J.P., Dai, Z., Joswiak, D., Browning, N.D., and Matrajt, G., 2009, The origin of refractory minerals in comet 81P/WILD 2: *Geochimica et Cosmochimica Acta*, v. 73, p. 7150–7161, <https://doi.org/10.1016/j.gca.2009.08.033>.
- Dobrzynetska, L.F., Wirth, R., Yang, J., Hutcheon, I.D., Weber, P.K., and Green, H.W., 2009, High-pressure highly reduced nitrides and oxides from chroitite of a Tibetan ophiolite: *Proceedings of the National Academy of Sciences of the United States of America*, v. 106, p. 19233–19238, <https://doi.org/10.1073/pnas.0905514106>.

- Drake, S.M., and Beard, A.D., 2012, Evidence from An Carnach, Strathaird Peninsula silicic pyroclastic deposits at the base of the Paleogene Skye Lava Field: *Scottish Journal of Geology*, v. 48, p. 133–141, <https://doi.org/10.1144/sjg2012-445>.
- Eldholm, O., and Grue, K., 1994, North Atlantic volcanic margins: Dimensions and production rates: *Journal of Geophysical Research*, v. 99, p. 2955–2968, <https://doi.org/10.1029/93JB02879>.
- Garai, J., Haggerty, S.E., Rekhi, S., and Chance, M., 2006, Infrared absorption investigations confirm the extraterrestrial origin of carbonado diamonds: *Astrophysical Journal*, v. 653, p. 153–156, <https://doi.org/10.1086/510451>.
- Grebennikov, A.V., 2011, Silica-metal spherules in ignimbrites of southern Primorye, Russia: *Journal of Earth Science*, v. 22, p. 20–31, <https://doi.org/10.1007/s12583-011-0154-0>.
- Heaman, L.M., and LeCheminant, A.N., 1993, Paragenesis and U–Pb systematics of baddeleyite (ZrO_2): *Chemical Geology*, v. 110, p. 95–126, [https://doi.org/10.1016/0009-2541\(93\)90249-1](https://doi.org/10.1016/0009-2541(93)90249-1).
- Jacquet, E., Alard, O., and Gounelle, M., 2015, The formation conditions of enstatite chondrites: Insights from trace element geochemistry of olivine-bearing chondrules in Sahara 97096 (EH3): *Meteoritics & Planetary Science*, v. 50, p. 1624–1642, <https://doi.org/10.1111/maps.12481>.
- Kyte, F., 1998, A meteorite from the Cretaceous/Tertiary boundary: *Nature*, v. 396, p. 237–239, <https://doi.org/10.1038/24322>.
- Leroux, H., Reimold, W.U., Koeberl, C., Hornemann, U., and Doukhan, J.-C., 1999, Experimental shock deformation in zircon: A transmission electron microscopic study: *Earth and Planetary Science Letters*, v. 169, p. 291–301, [https://doi.org/10.1016/S0012-821X\(99\)00082-5](https://doi.org/10.1016/S0012-821X(99)00082-5).
- Parnell, J., Mark, D., Fallick, A.E., Boyce, A., and Thackrey, S., 2011, The age of the Mesoproterozoic Stoer Group sedimentary and impact deposits, NW Scotland: *Journal of the Geological Society [London]*, v. 168, p. 349–358, <https://doi.org/10.1144/0016-76492010-099>.
- Reddy, S.M., Johnson, T.E., Fisher, S., Rickard, W.D.A., and Taylor, R.J.M., 2015, Precambrian reidite discovered in shocked zircon from Stac Fada impactite Scotland: *Geology*, v. 43, p. 899–902, <https://doi.org/10.1130/G37066.1>.
- Saunders, A.D., Fitton, J.G., Kerr, A.C., Norry, M.J., and Kent, R.W., 1997, The North Atlantic Igneous Province, in Mahoney, J.J., and Coffin, M.F., eds., *Large igneous provinces: American Geophysical Union Geophysical Monograph* 100, p. 45–93, <https://doi.org/10.1029/GM100p0045>.
- Timms, N.E., Reddy, S.M., Cavosie, A.J., Nemchin, A.A., Grange, M.L., and Erickson, T.M., 2015, Record of the early impact history of the Earth–Moon system: Targeted geochronology of shocked zircon [abs.]: *42nd Lunar and Planetary Science Conference*, p. 2190.
- Wu, X.L., Meng, D.W., and Han, Y.J., 2005, PbO_2 -type nanophase TiO_2 from coesite-bearing eclogite in the Dabie Mountains, China: *American Mineralogist*, v. 90, p. 1458–1461, <https://doi.org/10.2138/am.2005.1901>.
- Zhang, Y., and Sears, D.W.G., 1996, The thermometry of enstatite chondrites: A brief review and update: *Meteoritics & Planetary Science*, v. 31, p. 647–655, <https://doi.org/10.1111/j.1945-5100.1996.tb02038.x>.

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