THE PERMIAN-TRIASSIC BOUNDARY, KAROO BASIN, SOUTH AFRICA: GEOCHEMICAL INSIGHT INTO THIS MASS EXTINCTION EVENT. L. Coney¹, W.U. Reimold², P.J. Hancox¹, D. Mader¹, C. Koeberl², J. McDonald³, U. Struck², V. Vajda² and S.L. Kamo⁶, ¹School of Geosciences, University of the Witwatersrand, Private Bag 3, P.O. WITS, Johannesburg, South Africa (louise.coney@gmail.com), ²Museum for Natural History (Mineralogy), Humboldt-University, Invalidenstrasse 43, D-10115, Berlin, Germany, ³Dept of Geological Sciences, University of Vienna, Althanstrasse 14, A-1090, Vienna, Austria; ⁴School of Earth, Ocean and Planetary Sciences, Cardiff University, Park Place, Cardiff, CF10 3YE, U.K., ⁵Dept of Geology, GeoBiosphere Science Centre, Lund University, Sölvegatan 12, SE-223 62, Lund, Sweden, ⁶Jack Satterly Geochronology Laboratory, Dept of Geology, University of Toronto, 22 Russell Street, M5S 3B1, Toronto, Canada.

**Introduction:** The Permain-Triassic (P-Tr) mass extinction has been documented as the largest of the mass extinctions that took place in the Phanerozoic [1-2]. The cause of the extinction event has been the subject of much debate: theories proposed range from asteroid/comet impact [3-6] to volcanism [7-9], methane clathrate dissociation events [1; 10-11], oceanic anoxia [12-14], and combinations of these processes [15-19]. The Karoo Basin of South Africa contains a number of palaeontologically well-constrained terrestrial sections (particularly in the south and east of the Basin; [20]). Until recently, research on the P-Tr sections in the Karoo Basin was mostly of a palaeontological and sedimentological nature: the present study [21] has focused on fully characterising a number of sections geochemically and mineralogically.

**Study Area:** Two sections from the southern Karoo Basin (Commando Drift Dam and Wapadsberg, Eastern Cape Province, South Africa) have been evaluated geochemically and mineralogically. The Commando Drift Dam section has been constrained palaeomagnetically by a previous study [22]. The palaeomagnetic boundary (reversed to normal signatures) occurs approximately 5.3 m above the palaeontologically defined boundary [22]. Additionally, sedimentological and geochemical evaluation of a third section in the eastern Karoo Basin, Injusiti (Kwazulu-Natal Province, South Africa), has taken place. The sections comprise mostly mudstones, together with siltstones and sandstones. Carbonate nodular horizons have been noted in the southern Karoo sections. Each section is marked by an “event bed” at the stratigraphic position of the respective palaeontological boundary; this event bed comprises a centimeter to metre thick, laminated mudstone layer. All sections are characterized by a change in colour of the mudstones from green-grey to red-brown at the palaeontologically-defined boundary.

**Geochemistry:** No substantial changes related to the major and trace element geochemistry have been found in any section, and any changes relate either to the lithological changes (i.e., silica-rich rocks vs. carbonate nodular horizons) or to weathering effects. Iron content increases concomitantly with the colour change from green-grey to red-brown across the palaeontologically-defined boundary, and at the Commando Drift Dam section, a second maximum is attained at the palaeomagnetically defined boundary. The increase has been caused by post-deposition oxidation of Fe²⁺ to Fe³⁺, potentially caused by climatic warming, aridification or the influx of a post-depositional fluid; the last possibility may be rejected as there is the presence of red-beds at the boundary worldwide, which implies at least a regional, rather than local cause.

The Injusiti section shows similar geochemical characteristics to the southern Karoo sections, although there is a lack of carbonate nodular horizons. Additionally, there is relative enrichment in Na₂O and depletion in K₂O contents (by a few wt%) across the palaeontologically-defined boundary in this section. This is not observed in the southern Karoo sections, and is thought to represent local lithological variation.

Trace element variation largely reflects associated major element changes. Rare earth element concentrations do not change across the respective palaeontologically-defined boundaries in the two sections.

**Platinum Group Element (PGE) results.** The Commando Drift Dam section was evaluated for variation in PGE content in order to ascertain whether a possible enrichment due to meteorite impact had taken place: all analysed samples from above, at and below the palaeontologically constrained boundary had similar PGE contents, reflective of the background PGE contents found in clay-rich sediments. This is in agreement with other geochemical studies of P-Tr sections [23]. Additionally, no evidence for impact-generated microdeformation features were found, which agreed with the negative – with respect to impact - chemical results.

**Carbon isotope results.** The Commando Drift Dam section was measured for bulk and carbon isotope results. Samples from the Injusiti section were measured for their organic carbon signature. The bulk carbon isotope values revealed negative excursions (relative to background values) at both the palaeontological and palaeomagnetic boundaries. Both sections have comparable results for their organic carbon content, which is also similar to those reported from previous studies of P-Tr sections in the Karoo Basin [10, 24]. The cause of
the carbon isotope excursions is, as yet, unclear, but it can be mooted that the negative excursions were caused by a variety of contributions, including the Siberian Flood Basalts in addition to methane from other sources (e.g. coal beds [19] or the collapse of primary ocean productivity [25]). The contribution of massive methane clathrate dissociation is rejected, as this would have caused larger than observed carbon isotope excursion.

**Palynology:** Low diversity flora (composed of bryophytes, lycophytes and gymnosperms) have been reported from the Commando Drift Dam section. These forms are interpreted as traces of the surviving plants enduring the major extinction pulse. At, and above the level of the palaeomagnetic boundary only fungal spores are present, which is similar to patterns observed for the Cretaceous-Palaeogene boundary [26-27].

**Timing of the mass extinction in the Karoo Basin:** U-Pb age dating was performed on zircon crystals extracted from the event bed. The timing of the vertebrate extinctions in the Karoo Basin has so far not been determined, but one of the crystals analysed here yielded an age of 252.5 Ma. This age is in good agreement with the accepted age of the boundary [28-30], and provides a maximum constraint on the age of the event bed.

**Conclusions:** The combined geochemical and mineralogical study of rocks covering mass extinction events can provide valuable information elucidating (or rather refining) the causes of such a mass extinction. This study has shown that extinction caused by meteorite impact is seemingly not viable for the P-Tr mass extinction and that rather a complicated chain reaction of greenhouse gas emission leading to the mass extinction of fauna and flora took place.

**Acknowledgements:** This work was funded by: the Palaeo-Anthropology Scientific Trust, Johannesburg; the National Research Foundation of South Africa; the Geological Society of South Africa; the Barringer Family Fund for Meteorite Impact Research; the Swedish Research Council. Analytical work in Vienna was supported by the Austrian FWF, project P17194-N10 (to CK). Bernd Bodiselitsch (formerly University of Vienna, Austria) is thanked for assistance with some of the carbon isotope analysis.