A MINERALOGICAL AND GEOCHEMICAL STUDY OF THE NONMARINE PERMIAN-TRIASSIC BOUNDARY IN THE SOUTHERN KAROO BASIN, SOUTH AFRICA L.Coney[1], W.U. Reimold[1], P.J. Hancox[1], and C. Koeberl[2] [1]Impact Cratering Research Group, School of Geosciences, Univ. Witwatersrand, Private Bag 3, Johannesburg, Wits 2050, South Africa; [2]Dept. of Geological Sciences, University of Vienna, A-1090 Vienna, Austria (ConeyL@science.pg.wits.ac.za)

Summary: Mineralogical and geochemical investigations across two nonmarine Permian-Triassic (P/Tr) boundary sections in the southern part of the main Karoo Basin have been undertaken in order to aid in our understanding of this complex extinction event.

Introduction: The end-Permian (251.4 ± 0.1 Ma) mass extinction is universally acknowledged as the most consequential of the five major Phanerozoic mass extinctions. More than 90% of marine species, ~70% of terrestrial vertebrates and ~90% of plant life were lost in a very short timespan [1,2]. The nature of the P/Tr boundary and the cause of the mass extinction have been the subject of international debate. Possible causes for the P/Tr extinction include: asteroid/comet impact; environmental change; oceanic anoxia or overturn; volcanism and synergistic combinations of the above [3]. Occurrences of planar deformation features in quartz in Australian and Antarctic sections have been reported [4] but not yet confirmed. Iridium concentrations do not show a clear anomaly as seen in K/T boundary sections. A $\delta^{13}C$ negative excursion has been seen to accompany some inconsistent Iridium anomalies in marine sections [1]. Becker et al. [5] supposedly found evidence for impact, but this has been solidly refuted [6,7]. Kaiho et al. [8] used the coincidence of sulphur and strontium isotopic data and strange metallic grains to suggest the event was caused by impact-triggered release of mantle-derived sulphur and strontium, but this was rejected by Koeberl et al. [9] based on a number of different arguments. Evidence proposed for an exogenic play at the P/Tr boundary therefore remains contentious.

Evidence for a volcanic cause includes the eruption of the Siberian Flood Basalts at the time of the mass extinction [10,11]. The eruptions would have introduced large volumes of carbon dioxide and sulphide/ate [11] into the atmosphere, which could have triggered extensive acid rain [16]. The observed $\delta^{13}C$ excursion could have been caused by rapid release of methane or carbon dioxide coincident with the volcanic event.

The boundary is now well documented in the marine realm, however far less is known about the pattern and duration of the extinction event in the nonmarine realm, and as to whether these events are truly synchronous.

The Karoo Basin, South Africa: The Karoo Basin is a large retro-arc foreland basin which accumulated sediment from the Carboniferous (300 Ma) through to the Early Jurassic (180 Ma) in southwestern Gondwana. The Karoo Basin also preserves a largely uninterrupted 100 million year palaeontological record which has aided in the biostratigraphic subdivision of the sequence. From the end of the Middle Permian on, deposition in the Karoo Basin was puerely nonmarine[12], and the basin preserves a number of P/Tr boundary sections. Hancox et al. [13] have shown that the extinction event in the north of the boundary is marked by an erosional unconformity, however the sequence is temporally complete in the southern, more proximal reaches of the basin.

Historically the P/Tr boundary in the Karoo Basin has been placed biostratigraphically at the contact between the *Dicynodon* and *Lystrosaurus* Assemblage Zones [14], however Smith and Ward [2] have shown that the boundary is better placed at the Last Appearance Datum (LAD) of *Dicynodon*. This is because the First Appearance Datum (FAD) of *Lystrosaurus* actually occurs in the Permian. Ward et al. [3] have also documented a change in fluvial style across the boundary. A changeover in climate from an arid and highly seasonal (Permian) to semi-arid and less seasonal (Triassic) climate has been proposed on the basis of observations of palaeosol types in sections crossing the boundary in the Karoo Basin [15]. This is, however, in contrast to Smith [16], who believed the changeover marked a general drying of the floodplain. Coupled with changes in the carbon isotopes this may indicate a greenhouse-effect following the mass extinction. Previous authors have documented a synchronous global negative shift in carbon isotopic composition [18], however other authors [19] question this.

Recently, a section at Commandodrift Dam in the southern Karoo Basin has given reliable palaeomagnetic signatures [20], with a reversed-normal magnetic signal present, which co-incides with the palaeontologically defined boundary at this locality.

This study: Due to the uncertainty regarding the nature of the mineralogical and geochemical signatures across the P/Tr boundary in the Karoo Basin, two sections were sampled in the southern Karoo Basin where the sequence is most temporally complete. The first section was sampled across the interval of DeKock's [20] study, and the second across a

palaeontologically constrained boundary section at Wapadsberg.

Samples were taken at 2 cm intervals in the metre below and above the boundary, and in 25 to 50 cm intervals for the rocks below and above these. Geochemical analysis of the samples was done by XRF Spectrometry and INAA for major and trace elements, and mass spectrometry for carbon isotopes. Petrographic work is still in progress.

Lithological results: Both sections straddle the stratigraphic interval between the uppermost Palingkloof Member of the Balfour Formation and the lowermost part of the Katberg Formation. The lower part of the sequence is dominated by drab greenish-grey fines with smooth surfaced carbonate nodule horizons, and lenticular sandstone bodies that document a predominantly meandering environment. At both sections the end of the Permian is marked by palaeosol development, and a laminated mudrock layer (referred to as an event bed by Smith and Ward [2]). Above this event horizon, the fines become redder and the sandstones more laterally continuous with gutter cast erosional bases, documenting a change in fluvial style to one of a lower sinuosity.

Geochemical results: The carbonate nodular horizons in the lower part of the sequence are clearly indicated by the geochemical data, where increases in CaO are seen, with corresponding decreases in SiO_2 and Al_2O_3. For the Commandodrift Dam section, siderophile elements and Fe_2O_3 show the most variation, increasing in concentration where the mudrocks change colour from greenish-blue to red, indicating a more oxidizing, or a more Fe-rich environment (see Figure 1). This is not observed in the Wapadsberg section. The Fe_2O_3 concentrations decrease once the rocks change lithology back to sandstones, and then it increases once again when more mudstones are encountered. The trace elements are far more variable, with Cu concentrations increasing substantially (by ~10 ppm) at the proposed boundary site at Commandodrift Dam and slightly above it at Wapadsberg. Ni also shows an increase from approximately 15 ppm to 27 ppm; this remains high for the next 48 cm, and then decreases to 11 ppm, once sandstones are encountered in both sections. Co contents show irregular variations with no major increases or decreases for any particular lithology. Iridium values (by INAA) are below the detection limit for almost all samples and no Ir anomaly is observed for the sections studied.

Discussion and Conclusion: The change in colour and nature of the paleosols across the boundary in the southwestern Karoo basin observed by Retallack et al. [15], from red to greenish grey, is the same as seen in the Commandodrift Dam section. Increasingly quartz-rich compositions following the boundary are seen, indicating increasing chemical weathering, and this observation corresponds to the findings of Retallack et al. [15], as well as Hancox et al. [12] in the northern basin near Senekal. The suggestion of extinction by the degassing of methane from shallow marine and permafrost clathrates, supported by [15], cannot be confirmed in our study. The geochemical results for the two sections are inconclusive with regard to a dramatic change in environmental conditions at the P/Tr boundary as chemical characteristics below and above the palaeontologically and palaeomagnetically defined boundary seem to be similar, with the only chemical difference caused by the local presence of carbonate nodules.

Acknowledgements: This work is funded through the Palaeo-Anthropology Scientific Trust (PAST), the Geological Society of South Africa, and the Barringer Family Fund for Meteorite Impact Research. Analytical work in Vienna was supported by the Austrian FWF, project Y58-GEO (to CK).

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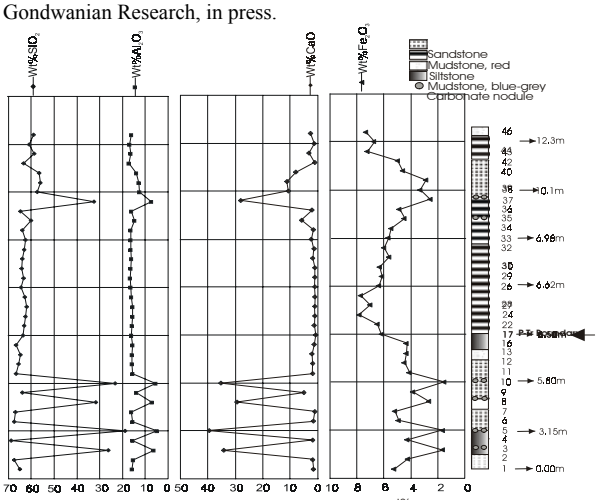

Figure 1