**APPLICATION OF CLUMPED ISOTOPE THERMOMETRY TO ARCHEAN CARBONATES: THERMAL HISTORIES AND POTENTIAL FOR BIOMARKER PRESERVATION .** N.P. Levitt[1,2], J.M. Eiler[1,3], N.J. Beukes[4], and C.M. Johnson[1,2], [1]NASA Astrobiology Institute, [2]Department of Geoscience, University of Wisconsin-Madison, 1215 W. Dayton Street, Madison, WI, 53706, USA, [3]Division of Geological and Planetary Sciences, California Institute of Technology, 150 S Mudd, MC 150-21, Pasadena, CA 91125, USA, [4]Department of Geology, University of Johannesburg, P.O. Box 524 Auckland Park 2006, Johannesburg, South Africa

**Introduction:** The Campbellrand-Malmani carbonate platform is located on the western margin of the Kaapvaal Craton of South Africa. This sequence has experienced the lowest grade thermal history of any Archean carbonate rocks, and is therefore an archive for records of the early Earth biosphere. However, current understanding of the burial history of these rocks is limited. Clumped isotopes can inform the search for and interpretation of biosignatures in sediments by determining host rock formation temperature and/or thermal history. This approach is especially attractive to studies of (organic) molecular biomarkers where alteration by excessive burial heating can obscure primary information.

Sumner and Beukes [1] have estimated platform burial by thermal subsidence to be from 0.8km/100my to 4.9km/300my between ~2.7 and ~2.5 Ga. The maximum burial temperature of the platform has been estimated by Miyano and Beukes [2] according to metamorphic mineral assemblages in the overlying Kuruman Iron Formation to be ~ 110-170 °C. Estimates of uplift and exhumation rates for the Kaapvaal Craton range from 4.4m/my to 800m/my and the timing of uplift has been recently been estimated between 75 to 30 Ma [3].

The objective of this study is to explore how the burial and exhumation history of the platform affected clumped isotope thermometry using the transient defect/equilibrium defect reording model of Henkes et al. [4] and the solid-state reaction-diffusion based model of Stolper and Eiler [5]. These models present kinetic data for calcite, and recent work indicates that dolomite re-equilibrates more sluggishly [6]. The approach taken here is to compare unique $^{13}C$-$^{18}O$ bond reordering kinetics in calcite and dolomite to help constrain the timing and duration of burial, thermal exposure, and exumation of this unique Archean archive.

**Investigation:** Clumped isotope analyses were performed on micro-drilled powder from hand samples and drill core collected from the Gammohaan Formation of the Campbellrand Subgroup. The majority of samples are from an outcrop from a hill near Kuruman. Samples from three drill core were also taken at depths ranging from ~200 m to ~290 m to test for spatial variability in petrographic textures and geochemical characteristics. Assuming a cratonic geothermal gradient of 20$^{o}$C/km, the drill core samples would have experienced slightly higher temperatures before sampling of ~ 5 $^{o}$C relative to the outcrop samples. Dolomite was not found in sufficient abundance in the drill core samples initially studied.

We explore burial from 2.55 to 2.40 Ga from ambient conditions to a range of peak temperatures from 150-250$^{o}$C. Under such conditions, calcite quickly attains the maximum temperature for clumped isotopes while dolomite slowly re-orders toward its blocking temperature of 300-350$^{o}$C [6]. Although some workers have argued for peak metamorphic conditions at ~2 Ga, the rapid equilibration of calcite would not change the results. Exhumation of the platform was modeled as occurring in the range from 200 to 30 Ma.

**Results and Conclusions:** $^{13}C$-$^{18}O$ bonding measurements were converted to temperatures using the calibration curve reported by Lloyd et al. [6]. Specimens where only early carbonate was sampled give apparent temperatures ranging from 114-173°C for calcite and 90-115°C for dolomite. Average values for calcite and dolomite were found to be 137°C (±20) and 99°C (±13), respectively.

Our modeled time-temperature histories below 200 $^{o}$C would produce clumped isotope compositions in the observed range. The models further call for a rapid exhumation of the basin of less than 200 million years. This uplift history is broadly consistent with estimates for the Kaapvaal Craton reported by previous investigators. These results indicate that for geologically reasonable exhumation rates, the final calcite clumped isotope temperature is ~20-60 $^{o}$C cooler than peak conditions. That these results are in line with the maximum metamorphic temperatures estimated below 200 $^{o}$C is encouraging for the reliability of primary biogeochemical signals extracted from the Campbellrand-Malmani carbonate platform.

**References:** [1] Sumner D.Y. and Beukes N.J. (2006) *Geol. Soc. S. Africa, 109,* 11-22. [2] Miyano T. and Beukes N.J. (1984) *Trans. Geol. Soc. S. Africa, 87*, 111-124. [3] Dauteuil O. et al. (2015) *Geomorphology 233*, 5-19. [4] Henkes G.A. et al. (2014) *Geochim. Cosmochim. Acta, 139*, 362-382. [5] Stolper D.A. and Eiler J.M. (2015) *Am. J. Sci., 315*, 363-411. [6] Lloyd M.K. et al. (2017) *Geochim. Cosmochim. Acta, 197*, 323-344.