ORIGINS OF PU/U VARIATIONS IN >4 Ga TERRESTRIAL ZIRCONS. E. A. Bell[1], J. D. Gilmour[2], T. M. Harrison[1], G. Turner[2], S. A. Crowther[2]; [1]Dept. of Earth and Space Sciences, UCLA (ebell21@ucla.edu), [2]School of Earth, Atmospheric, and Environmental Science, University of Manchester.

Introduction: Examination of radiogenic xenon in chondritic meteorites led to an estimation of solar system initial $^{244}Pu/^{238}U$ of ~0.007[1]. However, apparent initial Pu/U ratios in >4 Ga terrestrial zircons from the Jack Hills, Western Australia, yield variations both above[2] and below[2,3] this value. Given the highly variable behavior of Pu and U under even mildly oxidized aqueous conditions[4], this variation could be an indicator of aqueous alteration in the precursors to Jack Hills zircon magmas. This could be a second line of evidence (after high $\delta^{18}O$ values in the same zircons) for a Hadean hydrosphere[5], contrasting with the earlier paradigm of a dry Hadean Earth. However, the lack of extant natural plutonium has limited insights into its behavior in terrestrial geologic settings. Thus an aqueous history may not be the only potential cause of Pu/U variations, and the potential effects of magmatic evolution (similar to that seen in evolving zircon U/Th ratios) and secondary alteration of the zircons need to be considered. In order to unravel the causes of apparent Jack Hills Pu/U variations, we have collected a multivariate dataset on 11 zircons consisting of analyses of xenon isotopes along with U-Pb age, trace element contents, and oxygen isotopes. Consideration of the xenon-derived Pu/U estimates with other geochemical information on a wider suite of Jack Hills Hadean zircons suggests that Pu/U in the zircons reflects both secondary alteration and primary zircon chemistry derived from various processes operating on the Hadean Earth. Understanding these processes will yield insights for the interpretation of Pu/U signatures on planetary bodies in the early solar system.

Methods: U-Pb age, oxygen isotope analyses, and trace element analyses of 32 zircons were made on CAMECA *ims*1270 ion microprobes. Ages and $\delta^{18}O$ for 23 of the sampled zircons are reported in [6]. 11 Zircons were irradiated to induce fission of ^{235}U (similar to the procedure documented by [2]) at a nominal neutron fluence of ~5-6x10^{18} n/cm^2. Xenon isotopic analyses were made using the Refridgerator-Enhanced Laser Analyzer for Xenon (RELAX) instrument[7,8]. Zircons were heated with an infrared laser at various temperatures to extract xenon, resulting in one or several xenon release steps per zircon.

Results: *Mixture models based on other variables:* Finite mixture modeling of a larger dataset of 32 Hadean Jack Hills zircons using variables relevant to both aqueous alteration ($\delta^{18}O$, U/Th due to the solubility of U)[4,5] and magmatic differentiation (Zr/Hf, Yb/Gd and U/Th, T^{xlln})[9,10] along with $^{207}Pb/^{206}Pb$ age, Nd/U (due to similarities of Pu and Nd chemistry in some meteorite studies[11]), and U_t (to check for uranium abundance effects on its various ratios; the subscript 't' refers to the ratio at the time of zircon crystallization) suggests two groups of zircons, separated most readily by Nd/U_t. Group A have Nd/U_t > 0.009, range 4.16-4.09 Ga in age (average 4.12 Ga), and have significantly lower $(U/Th)_t$ and Yb/Gd. Group B ranges 4.2-4.0 Ga in age (average 4.07 Ga) and has significantly higher $(U/Th)_t$ and Yb/Gd. There is no appreciable difference in U_t or $\delta^{18}O$ between the groups. Group B contains all of the zircons with multiple xenon release steps as well as all of the zircons with $(Pu/U)_o$ > 0.001 in this dataset (the subscript 'o' refers to the ratio projected to the beginning of the solar system at 4.568 Ga).

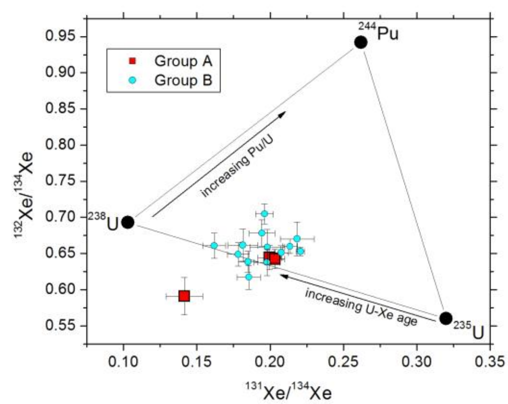

Fig. 1: Hadean zircon data in xenon three isotope space. All but one xenon release fall within error of a ternary defined by the end members produced by fission of ^{244}Pu, ^{238}U, and ^{235}U.

Xenon Results: Fig. 1 shows our 11 Hadean zircons in three xenon isotope space. All fall within a ternary consisting of the two radiogenic end-members (^{238}U and ^{244}Pu) and nucleogenic xenon from ^{235}U. The zircons' $(Pu/U)_o$ show only a weak correlation with $\delta^{18}O$ (see Fig. 2b; when only the highest-Pu/U release step in each zircon is considered, R^2~0.4) and no obvious correlations with indicators for melt evolution such as Ti-in-zircon crystallization temperature (T^{xlln}), $(U/Th)_t$, Zr/Hf, or Yb/Gd. However, $(Pu/U)_o$ does show a rough inverse trend with several LREE/actinide ratios, seen most clearly with Nd/U_t (Fig. 2a). High Nd/U_t values are associated exclusively with low $(Pu/U)_o$, and low Nd/U_t with both high and low $(Pu/U)_o$. This contrasts with the similar Pu and Nd chemistry in meteorites[11].

Discussion: The younger Group B set contains all zircons in this dataset with apparent $(Pu/U)_o$>0.001. It also appears to include zircons from more magmatically evolved systems (e.g., later-stage melts or more felsic granitoids). Earlier investigations of Jack Hills zircon xenon also revealed higher Pu/U generally falling among younger zircons[2], although there is no information on these zircons' trace element chemistries. The lack of $(Pu/U)_o$ correlations with other variables in this dataset may be due to the small sample size.

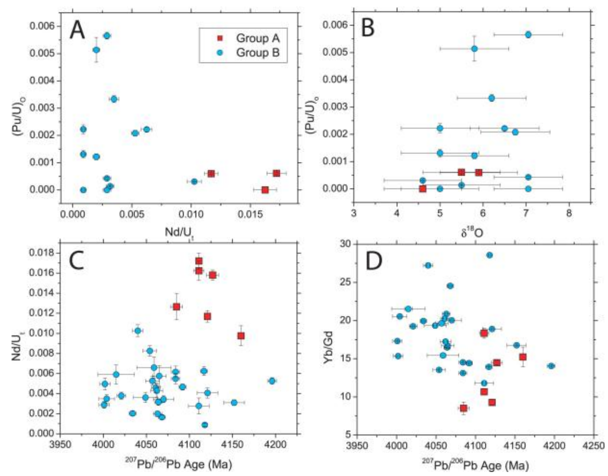

Fig. 2: Hadean Jack Hills zircons in several geochemical variables. Negative $(Pu/U)_O$ estimtes are shown here as zero. The zircons' apparent $(Pu/U)_o$ vs. Nd/U_t and the aqueous indicator $\delta^{18}O$ (A,B); Hadean zircons' $^{207}Pb/^{206}Pb$ ages vs. Nd/U_t (C) reveals that the high-Nd/U_t zircons are temporally restricted to ~4.15-4.1 Ga. Yb/Gd, an indicator for magmatic temperature and evolution, increases with time (D).

Effects of recrystallization on Pu/U: A notable feature of the older Group A is the bimodal nature of their relative U-Xe ages: Group A contains both one of the oldest and two of the youngest relative U-Xe ages (see Fig. 1). This higher degree of xenon loss compared to many younger Group B zircons could also explain some of the variations in Pu/U. An earlier study found that Pu/U divergence from a chondritic estimate of ~0.007[1] increases in Jack Hills zircons for increasing discordance between $^{207}Pb/^{206}Pb$ and U-Xe ages, indicating xenon loss as a method for generating Pu/U diversity.

A late loss of xenon due to heating or recrystallization would be expected to lead to both lower U-Xe age and apparent Pu/U. However, certain types of solid-state recrystallization[12] concentrate compatible trace elements in the zircon lattice, and such a process operating while Pu was still live would form Pu/U-enriched recrystallized regions. Lower U-Xe ages coupled with higher Pu/U for some release steps from multi-release zircons are observed both here and in a previous study[2]. This may point to such Hadean recrystallization events, although the timing remains unclear.

Secondary aqueous alteration: One explanation for the weak trend (R^2~0.4) between the highest-$(Pu/U)_o$ releases and the $\delta^{18}O$ of their respective zircons may be the production of both low-Pu/U and low-$\delta^{18}O$ regions in the zircons by later reaction with a hydrous fluid. Of our samples only one (ANU 31-15.8) displays the high, flat LREE pattern often interpreted as resulting from aqueous alteration[9]. However, both lower $\delta^{18}O$ and enriched LREE (for which we use Nd/U_t as a proxy) are expected results of secondary aqueous alteration, and so the association of lower $\delta^{18}O$ and $Nd/U_t > 0.01$ exclusively with low-Pu/U zircons may indicate that the low-Pu/U signature in these zircons is due to later aqueous alteration. The relatively young U-Xe ages resulting from later xenon loss in several Group A zircons provides further support for this interpretation. The timing of this proposed aqueous alteration event is difficult to estimate but an upper bound of ~4.0 Ga is constrained based on the youngest crystallization ages of zircons similar in relative U-Xe age to young Group B samples.

Primary variation in Group B: The differing Pu/U in different xenon release steps of three Group B zircons suggests secondary alteration, in general apparently including an enhancement of Pu/U in the younger release (and thus likely due to Hadean recrystallization of portions of the zircons). The rest of the $(Pu/U)_o$ variation may well be primary. The lack of any but weak trends between $(Pu/U)_o$ (highest release steps only) and various indicators for both aqueous activity and magmatic differentiation is either due to small sample size or the contribution of several processes to the primary Pu/U diversity. A larger sample set will be needed to determine the cause(s) of primary Pu/U variations in Hadean zircons.

References: [1] Hudson, G.B., et al. (1989) *Proc. 19th Lunar and Planetary Sci. Conf.*, 547-557. [2] Turner, G., et al. (2007) *Earth. Planet. Sci. Lett.* 261, 491-499. [3] Turner, G., et al. (2004) *Science* 306, 89-91. [4] Langmuir, D. (1978) *Geochim. Cosmochim.* Acta 42, 547-69. [5] Harrison, T.M. (2009) *Annu. Rev. Earth. Planet. Sci.* 37, 479-505. [6] Trail, D., et al. (2007) *Geochem.Geophys.Geosyst.*8, Q06014. [7] Gilmour, J.D., et al. (1994) *Rev. Sci. Instrum.* 65, 617-625. [8] Crowther, S. A., et al. (2008) *J. Anal. At. Spectrom.* 23, 938–947. [9] Hoskin, P.W.O. and Schaltegger, U., (2003), In Hanchar, J.M., Hoskin, P.W.O., eds., Zircon. *Rev. Mineral.* 53, 343-385. [10] Claiborne, L.L., et al. (2010) *Contrib. Mineral. Petrol.* 160, 511-531. [11] Jones, J.H, Burnett, D.S. (1987) *Geochim. Cosmochim. Acta* 51, 769-782. [12] Hoskin, P.W.O., Black, L.P. (2000) *J. Meta. Geol.* 18, 423-439.