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Climatic control on Quaternary coal fires and landscape evolution, Powder River basin, Wyoming and Montana

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Supporting Materials

Data

The sample numbers, locations, and zircon He ages are presented in Table S1. Most ages are weighted means of ages of multiple replicate analyses (typically 2-5) and uncertainties are standard errors. Some samples, however, comprise single analyses.

Lab Methodology

Dated grains were selected from mineral separates with Leica MZ16 stereozoom microscopes under both brightfield and darkfield, at 160-240x magnification. Grains were measured using digital cameras and image analysis software, to calculate alpha-ejection corrections and estimate parent and daughter nuclide concentrations. Alpha-ejection corrections for zircon were made following methods in the paper by Hourigan et al. (Hourigan et al., 2005). Grains were wrapped in Nb foil “microfurnaces” for laser heating (House et al., 2000). Crystal-bearing foil packets were heated by Nd:YAG laser to extract He gas, which was then spiked with ^{3}He. Helium contents were measured with an electron multiplier in a quadrupole mass spectrometer, and calculated from interference-, background-, and procedural-blank-corrected 4/3 ratios by reference to an on-line, manometrically calibrated ^{4}He standard. Linearity of the referencing has been confirmed over a 10^{3}-fold intensity range. Corrected 4/3 measurements on reference standards vary by less than 0.5% (1σ). Procedural blanks measured by lasing/heating empty foil packets are typically 0.05-0.1 fmol ^{4}He.

Following He measurement, foil packets were retrieved, transferred to Teflon vials, and spiked with ^{233}U and ^{229}Th. All samples were dissolved directly from foils in HF-HNO_3-HCl in high-pressure digestion vessels. Natural-to-spike isotope ratios were measured on a high-resolution (single-collector) Element2 ICP-MS. Precision on measured ratios for single grain apatites were generally 0.1-0.5% RSD, and analytical uncertainty on the isotope dilution measurements were typically <1.5% (1σ). Routine U-Th procedural blanks for zircon are 2.6 ± 0.5 pg U and 5.5 ± 1.0 pg Th (for more information see Reiners and Nicolescu (2006): http://www.geo.arizona.edu/~reiners/arhdl/arhdlrep1.pdf).

Propagated analytical uncertainties for most zircon samples lead to an analytical uncertainty on (U-Th)/He ages of approximately 1-3% (1σ). In some cases, actual observed reproducibility of multiple aliquots approaches analytical uncertainty (e.g., 2.6% (2σ) for 150 ka zircons (Blondes et al., 2007), and 2.3% (2σ) for gem-quality zircons (Nasdala et al., 2004)). In general, however, reproducibility of repeat analyses of (U-Th)/He ages is significantly worse than analytical precision. Cooling ages of zircon from igneous rocks typically show scatter on the order of one standard deviation of at least 6%, and in many cases more than 10%. This has several possible origins, including variable He diffusion characteristics among grains, unidentified intracrystalline inclusions that prevent complete U-Th-Sm recovery following degassing, or petrographic siting effects such as He implantation from adjacent high-U-Th phases or varying He retention due to varying diffusivity or partitioning of surrounding phases. As discussed above, however, it is likely that a major origin of the observed poor reproducibility comes through uncertainty in the alpha-ejection correction (Farley et al., 1996)—not from uncertainty in actual dimensions of dated grains, but uncertainties in relating observed grain boundaries of dated aliquots to original boundaries in the host rock, implantation from other phases, and inhomogeneous distribution of parent nuclides in dated grains (Farley et al., 1996; Hourigan et al., 2005; Reiners et al., 2004). It is extremely difficult to estimate, *a priori*, the expected magnitude of error arising from any of these potential sources. Thus He ages typically show a much greater scatter and higher MSWD than expected based on analytical precision alone, so multiple replicate analyses of (U-Th)/He ages on several aliquots is necessary for confidence in a sample's age. In this study, for zircon He age uncertainty we adopted the larger value among the propagated analytical uncertainty, or else 8%, the latter based on observed reproducibility of other typical igneous zircons.

T-test Methodology

We test the statistical relationship between a given paleoclimate time-series and clinker ages by comparing average paleoclimate conditions during clinker formation from average paleoclimate conditions for the full time-series.

We first create a synthetic data set of clinker ages to account for age uncertainties. We use a bootstrap algorithm in which, for each iteration of the algorithm, a new age for each clinker sample is chosen. We use a pseudo-random number generator that chooses each value from a normal distribution that is centered about each nominal clinker age and is scaled by the age error. Next, the paleoclimate value (e.g., eccentricity, $\delta^{18}O$) for that age is determined. We therefore have two data sets: the paleoclimate values corresponding with the times clinker formed, and the paleoclimate values for the entire paleoclimate time-series.

For each iteration, we use a *t*-test to assess whether the mean paleoclimate values when clinker formed, $\overline{X}_{clinker}$, are significantly different from mean paleoclimate conditions for the entire time-series, $\overline{X}_{all}$. The *t*-value is assessed using the equation

$$t_{clinker} = \frac{\overline{X}_{clinker} - \overline{X}_{all}}{\sqrt{\sigma^2_{clinker} / n_{clinker} + \sigma^2_{all} / n_{all}}} \qquad (1)$$

where σ^2 is the variance of each data set and n is the number of samples in each data set. The larger the magnitude of $|t_{clinker}|$, the greater the difference between $\overline{X}_{clinker}$ and $\overline{X}_{all}$, and the greater the likelihood that clinker preferentially forms during particular climatic regimes. The suite of bootstrap iterations allows assessment of the mean and standard deviation of $t_{clinker}$, presented in Table 1 of the manuscript.

The probability *p* of a Type I error in which we reject the null hypothesis $\overline{X}_{clinker} = \overline{X}_{all}$ for each paleoclimate time-series, is determined from two-tailed *t*-test tables. We confirm this result using a second synthetic data set in which $n_{clinker}$ random ages are chosen between 0-1.1 Ma, and t_{random} is assessed. The stated *p*-values match the probability that $t_{random} > t_{clinker}$ for each time-series. We also use the random ages to assess the probability of random ages producing, for all six paleoclimate records, *t*-value directions (i.e., positive or negative) indicating coal fires occurred during warm climatic states (i.e., times of intense summer insolation, low global ice volume, and warm Pacific Ocean temperatures). Because this is an exploratory study in which we are more interested in the relative magnitude of *t*-values than the absolute significance, we do not correct for multiple comparisons. However, even with a conservative Bonferroni correction, the *t*-value for eccentricity would be significant at α=0.05.

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Table DR1. Clinker sample locations and ages

Sample	Northing	Easting	Elevation (m)*	Age (Ma)	2σ error (Ma)	Replicates
06PRB01	4804917	471785	1488	0.016	0.006	2
06PRB02	4810467	478859	1447	0.007	0.006	2
06PRB03	4810244	478856	1434	0.115	0.008	2
06PRB04	4809052	482305	1473	0.249	0.023	1
06PRB05	4808952	482286	1509	0.096	0.006	2
06PRB06	4812123	483588	1440	0.213	0.012	2
06PRB07	4821007	485949	1494	0.211	0.012	2
06PRB08	4822156.3	491148.4	1565	0.219	0.009	2
06PRB09	4925125	468548	1353	0.105	0.005	2
06PRB10	4925577.4	468390.8	1352	0.133	0.006	1
06PRB11	4926873	466914	1359	0.114	0.005	2
06PRB12	4925570	475909	1428	0.191	0.008	2
06PRB13	4925635	475964	1430	0.188	0.011	2
06PRB16	4941731	469533	1362	0.211	0.012	3
06PRB19	5035793	460803	1050	0.014	0.005	1
06PRB20	5044859	430160	1212	0.089	0.013	1
06PRB21	5047075	430365	1314	0.308	0.025	1
06PRB24	5046546	430906	1223	0.014	0.002	2
06PRB25	5064321	423865	1241	0.120	0.006	2
06PRB26	5063059	424177	1229	0.515	0.019	3
06PRB27	5062392	424271	1243	0.217	0.127	1
06PRB29	5059895	425104	1245	0.326	0.016	3
06PRB38	5048450	401454	938	0.227	0.013	2
06PRB44	5033171	414882	1083	0.237	0.017	2
06PRB47	5017828	404008	1193	1.113	0.040	2
06PRB49	5007344	398994	1167	0.127	0.020	2
06PRB50	5002579	387175	1138	0.270	0.021	2
06PRB51	4998485	382222	1106	0.239	0.015	2
03NPRB01	4991027	357593	1059	0.013	0.001	2
03NPRB03	5056562	407988	1286	0.652	0.026	4
03NPRB04	5056178	408009	1200	0.110	0.009	1
03NPRB05	5055618	407812	1107	0.155	0.009	2
03NPRB06	5049133	406130	995	0.287	0.023	1
03NPRB14	5044292	398714	904	0.056	0.004	2
03NPRB16	5058402	380681	1297	1.073	0.086	1
03NPRB18	5054391	379947	1262	0.105	0.005	3
03NPRB19	5055093	387415	1302	0.981	0.039	4
03NPRB22	5068114	399197	911	0.603	0.028	3
03NPRB25	5048026	404138	917	0.152	0.012	1
638-2	5335999	537373	665	0.144	0.014	2
CLK1	4825072	490576	1528	0.205	0.012	2
CLK5	4838614	492079	1550	0.536	0.025	3
CLK6	4832988	483766	1453	0.127	0.010	1
CLK7	4930776	357758	1416	0.019	0.001	2

Sample	Northing	Easting	Elevation (m)*	Age (Ma)	2σ error (Ma)	Replicates
CLK8	4912347	377863	1428	0.117	0.007	2
CLK9	4882411	470401	1361	0.013	0.002	2
PRB11	4823950	486370	1500	0.010	0.001	2
PRB12	4823787	489538	1532	0.120	0.007	2
PRB15	4820745	492990	1559	0.216	0.012	2
PRB17	4822765	495900	1602	0.615	0.035	2
PRB18	4822594	495800	1601	0.550	0.031	2
PRB19	4822695	494515	1593	0.502	0.028	2
PRB20	4836235	460503	1539	0.024	0.001	2
SPL2	4836221	487925	1440	0.482	0.027	2
SPL3	4836273	485855	1439	0.198	0.011	2

*Elevation determined from National Elevation Dataset 1” digital elevation model.