## Halogen (F, Cl, Br, and I) systematics in mineralized and non-mineralized Upper Permian Longtan Formation coal from China

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Knowledge of the distribution, origin, and mode of occurrence of halogens in coal is becoming increasingly important as these elements can play a major role in flue-gas Hg speciation and boiler combustion and operation. We have examined F, Cl, Br, and I abundance in mineralized and nonmineralized coal from Guizhou and adjacent Provinces, southwestern China. All samples are Upper Permian Longtan Formation; non-mineralized and mineralized coals are bituminous and anthracite in rank, respectively. In mineralized coal, Carlin-type gold ore-forming solutions precipitated high amounts of As, Sb, Hg, and Au. Total F, Cl, Br, and I were determined by routine PGNAA and INAA methods. We also determined total S, ash yield, As (as a measure of mineralization), and potassium.

Very few significant correlations, either positive or negative, were found among the various parameters. In the mineralized coal, Cl correlates positively with Br, and F correlates positively with K and ash yield, no other correlations were significant. In the non-mineralized coal, we observed no significant correlations among the studied parameters. However, in general, F (mean = 444 ppm, maximum = 2266 ppm) and Br (mean = 29 ppm, max. = 100ppm) are higher in the mineralized coals; whereas, I (mean = 7.1 ppm, max. = 28 ppm) and Cl (mean = 164 ppm, max. = 564) are higher in the non-mineralized coals. Total sulfur content appears unrelated to any halogen distribution. In the mineralized coals, F is related to potassium suggesting that this element was fixed by clays. Iodine and S are usually indicative of sea-water influence, however, the highest I contents were in coals with the lowest total S that ranges from 0.1 to 0.4 wt%.

## Early archean crustal evolution from Jack Hills Detrital Zircons

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Although detrital zircons from Jack Hills, Western Australia, range from 3.1 to 4.37 Ga, most previous work has focused on the >4 Ga portion of the population. The age distribution, Lu-Hf and oxygen isotope systematics, and crystallization thermometry of the younger zircons provide a basis for comparison for pre- and post-4 Ga magmatic environments and may provide an important constraint on styles of early Archean crustal evolution. Differences in the oxygen systematics or crystallization temperatures  $(T^{\text{xlln}})$  with age could indicate changing magmatic conditions in the zircons' sources with time. Similarly, changing Hf T<sub>DM</sub> model ages could indicate different pre-magmatic source histories (depleted vs. enriched magma sources). Such information could be used to evaluate the null hypothesis of unchanging magmatic environment with time in the Jack Hills zircon source (s). The zircon record contains two essentially continuous age groups at 3.3-3.6 Ga and >3.8 Ga, with an age minimum separating the two. Analysis of ~70 zircons (fewer for some variables) in the 3.8-4.0 Ga period suggest similarities with the >4.0 Ga distribution [1] in  $\delta^{18}$ O, Hf T<sub>DM</sub> [2] and  $T^{\text{xlln}}$  with somewhat more low  $T^{\text{xlln}}$  values. The 3.3-3.6 Ga zircons have similar means in  $\delta^{18}$ O and  $T^{\text{xlln}}$ , but younger  $T_{DM}$  from 3.8-4.25 Ga<sup>2</sup>.  $\delta^{18}$ O and  $T^{xlln}$  are less variant among 3.3-3.6 Ga zircons, likely indicating less diverse sources or processes represented in the provenance. The few zircons in the range 3.6-3.8 Ga are insufficient at present for comparison with other age groups. We suggest that these similarities and differences among zircon age populations are best explained by considering the 3.3-3.6 Ga and >3.8 Ga zircons to represent distinct genetic populations - either that the two populations represent unrelated tectonic terranes or the younger zircons are related only to a subset of the older crust that produced >3.8Ga zircons. The alternative, null hypothesis is best tested by a massive analysis campaign to identify and then characterize 3.6-4.0 Ga zircon, especially for Hf  $T_{DM}$ .

[1]Harrison *et al.* (2008) EPSL pp. 476–486 <sup>2</sup>Bell *et al.* (2010) submitted to Chem. Geol.