Advances in zircon U-Pb geochronology: The Ludwig factor

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Over the past few decades, zircon U-Pb geochronology has made tremendous strides in terms of analytical capabilities. Many workers have contributed to a wide range of improvements, ranging from zircon grain selection strategies, to zircon pre-treatments, blank reductions, improved ionization efficiency, better calibration of isotope tracers, preparation and international distribution of such tracers, improved isotopic composition standards, etc. As a result, many labs now can analyze single zircon grains with accuracy and reproducibility that simply was not possible in the past.

Advances of the type noted above commonly get considerable attention. But it is crucial that we recognize the parallel (and closely interwoven) advances in statistical analysis that have been predominantly driven by Ken Ludwig. For many years Ken has recognized shortcomings in the way the community has handled data analysis, educated us about the shortcomings, and provided solutions in the form of 'Isoplot'. For many workers, the appearance of a new feature in Isoplot (e.g. taking U decay constant uncertainties into account in calculating concordia intercept errors) might have been the first inkling that there even was a 'problem'.

As analytical precisions have improved, Ludwig's rigorous statistical analyses have become especially important in avoiding overly optimistic interpretation of age accuracies. This in turn has led directly to development and acceptance of further improvements in analytical methods. Zircon U-Pb geochronology is widely regarded as the 'gold standard' of geochronology (at least by those of us who do zircon U-Pb analyses!). Ken Ludwig's career contributions are an integral and major part of this reputation.

Nanosims studies of $\delta^{15}N$ and $\delta^{13}C$ in nitrides inclusions in coesite from a Tibetan massive cromitite ore

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The Cameca NanoSIMS 50, a nanometer scale secondary ionization mass spectrometry, was used to measure nitrogen and carbon isotopes in recently discovered osbornite (TiN) and cubic boron nitride inclusions in coesite from the Luobasa massive chromitite ore of a Tibetan ophiolite [1]. We present here coordinated NanoSIMS-TEM-EELS studies that provided a unique opportunity to obtain simultaneous information on the isotopic and chemical compositions, and minerals structure on these same FIB-prepared foils. The TEM-EELS studies revealed presence of high-pressure minerals: polycrystalline aggregates of coesite after stishovite, TiO_2-II, TiN and cubic BN associated with $Fe°$, Fe-Ti alloy and an amorphous phase of unknown stoihiometry [1, 2]. Four replicate analyses of TiN made by NanoSIMS yielded isotopic compositions of $\delta^{15}N$ = -10.4 ± 3.0 ‰ and $\delta^{13}C$ = 5 ± 7 ‰; uncertainties are two standard errors. No variations in N and C isotopic composition were detected outside analytical uncertainty. The N isotopic composition of the inclusions suggests that the N is mantle-derived. Most upper mantle rocks have $\delta^{15}N$ = -5 ± 2 ‰ whereas atmosphere, ocean and crust have positive $\delta^{15}N$ up to +12 ‰ [3]. Our isotopic results are inconsistent with recycled continental material, and are comparable to much more negative $\delta^{15}N$ values (e.g. [4]) suggesting the presence of a ^{15}N-depleted deep mantle reservoir. We propose that presence of high-pressure inclusions of oxides and nitrides, along with mantle N-isotopic composition of the nitrides indicate that a potential precursor to the host Cr-spinel was an ultra-deep CF-type Cr-spinel polymorph with the calcium-ferrite structure ($Ca^{2+}Fe^{3+}_2O_4$). Presence of highly reduced minerals, nitrides and $Fe°$, suggest that part of deep mantle (>300km) is characterized by low fO_2 environment.

[1] Dobrzhinetskaya et al. (2009) PNAS 106, 19233–19238. [2] Yang, J.S. et al. (2007) Geology 35, 875–878. [3] Marty et al. (2003) EPSL 206, 397–410. [4] Cartigny et al. (1997) Terra Nova 9, 175–179.