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## Mass spectrometry in cluster science: Formation of cluster ions, magic number clusters and their fragmentation studies by tandem mass spectrometry

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Mass spectrometry in combination with an electrospray ion source provides an efficient and a powerful method for generating ionic clusters and studying their structure and characteristics. We have produced cationic and anionic clusters of lithium formate and studied their fragmentations by tandem mass spectrometry (collision-induced dissociation with $N_2$). Singly as well as multiply charged clusters were formed in both positive and negative ion modes with the general formulae, $(HCOOLi)_n\ Li^+$, $(HCOOLi)_n\ Limm^+$, $(HCOOLi)_n$ HCOO- and $(HCOOLi)_n\ (HCOO)_m^{m-}$. Several magic number cluster ions were observed in both the positive and negative ion modes although more predominant in the positive ion mode with $(HCOOLi)_3\ Li^+$ being the most abundant and stable cluster ion. Quantum chemical calculations were performed for smaller cluster ions that showed the trimer ion has a closed ring structure similar to the phenalenylium structure with three closed rings connected to the central lithium ion. Further additions of monomer units result in similar symmetric structures for hexamer and nonamer cluster ions.

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## Pb baddeleyite geochronology by the thermal extraction-thermal ionization mass spectrometry, a new method for dating Proterozoic large igneous provinces

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The ability to easily obtain precise (~0.1%) age determinations on mafic rocks can facilitate identification of contemporaneous magmatic events across continents and hence open new avenues of research investigations related to large scale mantle processes. We present high precision Pb age determinations on baddeleyite (ZrO2), a common accessory mineral in mafic rocks using thermal extraction-thermal ionization mass spectrometer (TE-TIMS). Replicate analyses of twelve preheated (at 1250 °C) and silica embedded baddeleyite grains from the Paleoproterozoic Phalaborwa carbonatite using this procedure have yielded a $^{207}Pb–^{206}Pb$ weighted mean age of 2060.3 ± 0.4 Ma, consistent with previously reported $^{207}Pb–^{206}Pb$ ages for this carbonatite occurrence determined by the conventional U–Pb isotope dilution-thermal ionization mass spectrometry (ID-TIMS) technique. Fourteen baddeleyite fractions from a large Paleoproterozoic N–S striking mafic dyke swarm in the Dharwar craton yielded a $^{207}Pb$–206Pb weighted mean age of 2215.9 ± 0.3 Ma, also consistent with previously determined conventional ages. All data were corrected for mass fractionation of 0.18%/amu as determined previously on zircon. Both data sets scatter outside measurement errors, implying an external 2 sigma error of 0.055% in the case of the carbonatite and 0.043% for the mafic dyke, which we suggest represents the reproducibility of the fractionation correction. Our results demonstrate that thermal extraction $^{207}Pb–^{206}Pb$ ages are comparable with the conventional U–Pb ages in both accuracy and precision. This new procedure does not need ultra-clean laboratory conditions (<1pg procedure blanks), a prerequisite for conventional high precision U–Pb geochronology, and hence can be easily practised in most TIMS isotope geochemistry laboratories.

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