FT-ICR/MS and quantum chemical studies of aqueous polyoxometalates

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Mass spectrometric and quantum chemical studies of aqueous oxometalates, for instance, polyoxotungstate and polyoxomolybdate clusters, provide a suitable means of delivering molecular-scale information on the speciation, distribution and abundance of such moieties in crustal fluids. This study presents Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric data pertaining to the stability of polyoxomolybdate and polyoxotungstate clusters as well as mixed polymolybdotungstate clusters. We also report theoretical geometries and energies of the above clusters using B3LYP/aug-cc-pVDZ level theory in combination with SDD ECPs for W and Mo. Ion cluster experiments have been conducted on a Bruker 7T FT-ICR mass spectrometer with electrospray ionization capability. The mass spectrometer has also been modified to include a leak valve system used to introduce solvents and conduct solvation studies of ion clusters. Ion clusters generated from electrosprayed aqueous solutions containing Na_2MoO_4 and Na_2WO_4 salts (1-50mM) include the polyoxomolybdates $[Na_{2m+1}Mo_mO_{4m}]^+$ ($m \leq 11$), polyoxotungstates $[Na_{2n+1}W_nO_{4n}]^+$ ($n \leq 20$), and the mixed polymolybdotungstates $[Na_{2(m+n)+1}Mo_mW_nO_{4(m+n)}]^+$ ($m+n \leq 5$) (see below). We also identified several gas-phase polyoxometalates with magic numbers (abundance anomalies) as well as pure and mixed doubly- and triply-charged polyoxometalate clusters. Thermodynamic data obtained for the stepwise solvation of individual polyoxometalate clusters with H_2O will be presented and compared with hydration energies obtained from quantum chemical calculations.

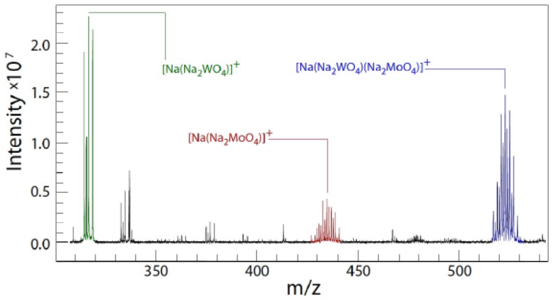

Figure 1: Positive-ion ESI-MS of aqueous Na_2MoO_4/Na_2WO_4 solution.

Mineralogy of the sodic-calcic hydrothermal alteration host rocks of the Esfordi, Choghart and Chadormalu magnetite-flourapatite deposits, Bafq area, Central Iran

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The Esfordi, Choghart and Chadormalu Ap-Mt deposits are located in the bafq area, Central Iran. Flourapatite is one of the most important mineral in the studied area. This mineral is formed in primary and secondary generations. On the basis of the EPMA analysis, flourapatite is characterized by high CaO (54-57), P_2O_5 (40-43) and minor amount Na_2O, SiO_2, F, Cl contents. Amphibole is the major mineral in the igneous rocks, sodic-calcic alteration and mineralization zones. This mineral has been found both phenochryst and needle inclusions in the apatite, magnetite, plagioclase and quartz minerals. The phenochryst of amphibole has altered to the brown biotite, chlorite and calcite. Chemically, two different amphiboles occur in the sodic-calcic alteration zone. The first type is edenite to ferro-edenite in the contact of igneous rocks, which has replaced by altered bodies. It has Na+K > 0.5 %, Mg# values 0.46 and highest Ti, AlVI values. The second type amphibole occurs in the sodic-calsic alteration zones and commonly replaced edenite with Na+K<0.50 and Mg# values of 0.67. The composition of them is between actinolite to magnesiohornblende. Also amphibole is a very important mineral in the mineralization zone. Chemically, it is actinolite to ferro-actinolite with average Mg# values of 0.57. On the basis of the palagioclase-amphibole geothermometer (Holland and Blundy 1994) this assemblage has formed in the 525-549° C and 1.2-1.7 kbar pressures, so evolution of the main hydrothermal process has occur in the shallow crust levels.

[1] Holland, T and Blundy, J., (1994) Non-ideal interactions in calcic amphiboles and their bearing on amphibole–plagioclase thermometry. *Contributions to Mineralogy and Petrology* **116**, 443–447.