

## 3.6.23

### Molybdenum solubility and transport under hydrothermal-magmatic conditions

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#### Molybdenum in porphyry deposits

Economic amounts of molybdenum are mainly found in Climax-type porphyry Mo deposits and as by-product in porphyry Cu deposits. Molybdenite mineralization generally occurs in quartz-molybdenite veins at temperatures of 500–650°C, inferred from fluid inclusions (1). There is some debate on the complexation and solubility of Mo in general and under magmatic-hydrothermal conditions no experimental data exist. To better understand and constrain the solubility and complexation of Mo experiments are conducted at high temperature and pressure.

#### Molybdenum solubility in synthetic fluid inclusions

Molybdenum solubility was investigated at 2 kbars over the temperature range of 500 to 800°C. Redox conditions were controlled by NNO, HM, and ReReO buffers. To determine the likely ligands of molybdenum transport under these conditions, experiments were run with starting solutions of different KCl concentrations (<5, 11, 38, 56 wt%) or pure H<sub>2</sub>O. Mo powder in Cl-bearing experiments and MoO<sub>3</sub> powder in H<sub>2</sub>O-bearing experiments were loaded in excess. In most of the experiments the pH was controlled by the qtz-mus-fsp mineral buffer. The experiments were run in cold-seal envelopes using Au and Pt capsules.

Fluid inclusions were trapped at high P and T in pre-fractured quartz rods and subsequently analyzed by laser ablation inductively-coupled plasma mass spectrometry (LA ICPMS). Fluid was extracted after the experiments of some runs and analyzed by ICP-AES. The results indicate that Mo is transported as hydroxyl complexes (e.g., H<sub>2</sub>MoO<sub>4</sub>). Despite the fact that Mo is a hard acid according to Pearson's principle it forms complexes with Cl to some degree, and the solubility increases with increasing salinity. Absolute solubility concentrations range between a few hundred ppms with slightly higher solubilities in H<sub>2</sub>O-bearing runs. No change in solubility was observed under different redox conditions, however, the blue colour of the fluid from an experiment at 500°C under NNO conditions indicates the presence of a mixture of Mo<sup>3+</sup> and Mo<sup>6+</sup> hydrolysis species.

#### References

- [1] W. H. White *et al.*, *Economic Geology*, 75th Anniversary Volume, 270–316 (1981).

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### The solubility of molybdenum in water vapour at elevated temperature and pressures

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The solubility of molybdenum trioxide in liquid-undersaturated water vapour has been investigated experimentally at 320°C and 80 to 100 bars. Experiments were conducted in solid titanium autoclaves loaded with powdered MoO<sub>3</sub> and a known amount of nanopure water. To prevent contact between the solid sample and the liquid water, the sample was contained within inert quartz glass ampoules supported by quartz glass holders. The volume of water in the system was pre-determined so as to preclude water saturation. The system was heated at 320°C until equilibrium was attained, then quenched to room temperature. The resulting condensate was analyzed for total Mo content by ICP-MS.

Results of these experiments show that the solubility of molybdenum in the vapour phase is between 6 and 9 ppm and increases linearly with P<sub>H<sub>2</sub>O</sub> (fig. 1). The dependence on P<sub>H<sub>2</sub>O</sub> is attributed to the formation of a hydrated molybdenum trioxide gaseous species, interpreted to have a hydration number of 1. The formation of the proposed complex can be described by the reaction:

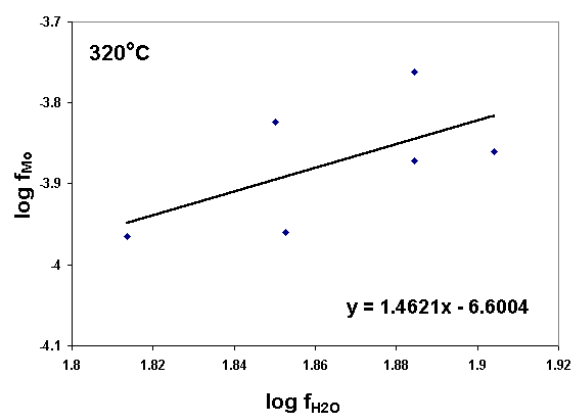
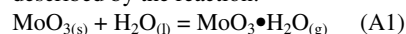


Fig. 1: Fugacity of Mo as a function of fugacity of water

Calculations based on the measured solubility of molybdenum at 320°C and the average H<sub>2</sub>O and total S fluxes at actively degassing volcanoes indicate that Mo-bearing water vapour can, in principle, form a deposit of 240 Mt, with an average grade of 0.15% Mo (e.g., the Endako Mo-porphyry deposit, Canada), within 8,000 years.