# The effects of sodium and chlorine on the solubility of molybdenum in aqueous vapour

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There is growing evidence that the solubility of Mo in water vapour may be high enough for metal transport in the vapour phase to be an important mechanism in the formation of porphyry Mo deposits (Rempel *et al*., 2006). Molybdenum is typically considered to be transported as a hydrated oxide, but research on Mo speciation in $H_2O$-free vapour suggests that the formation of Mo oxychlorides and sodium molybdates may be important (Hultgren and Brewer, 1956; Choudary *et al*., 1975). This study reports the results of experiments designed to investigate the effects of Na and Cl on Mo solubility in high-temperature water vapour.

The experiments were conducted in NaCl- and HCl-bearing aqueous vapour at 350°C and 60-160 bars. At $f$HCl<0.5 bars, Mo concentration appears to be independent of $f$HCl. However, at fugacities of HCl typical of volcanic gases ($f$HCl from 0.5 to 5 bars), the sum of the fugacity of Mo species increases with increasing $f$HCl in a ratio of ~1:2. At all fugacities of HCl, $\Sigma f$Mo species increases with increasing $fH_2O$ in a ratio of 1:2. These observations suggest that the predominant Mo species in the HCl-$H_2O$ system is a hydrated chloride or oxychloride. In the case of the former, the stoichiometry would likely be $MoCl_2 \bullet 2H_2O$, whereas the latter could be $MoO_2Cl_2 \bullet 2H_2O$, a species that has been reported to occur in HCl gas (Hultgren and Brewer, 1956). The sum of fugacities of Mo species in NaCl-bearing vapour rises linearly with increasing $\Sigma f$Na species in a ratio of 3:4. Furthermore, $\Sigma f$Na species is about two orders of magnitude higher than predicted for the partitioning of NaCl between $H_2O$ liquid and vapour (Bischoff 1991), indicating that the dominant Na species in the vapour is not NaCl. Values of $\Sigma f$Mo also increase linearly with $fH_2O$ (in a ratio of 1:3), suggesting the formation of hydrated Na molybdates. The ratio of $\Sigma f$Mo to $\Sigma f$Na of 3:4 implies the formation of two or more hydrated Na molybdates, e.g. $Na_2MoO_4 \bullet 3H_2O$ or $NaHMoO_4 \bullet 3H_2O$.

The results of this study, in conjunction with the known elevated concentrations of Na and Cl in magmatic vapours, suggest that such vapours are more than capable of dissolving the concentrations of Mo required to form porphyry Mo deposits.

## References

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# Molecular identification of the Deuterium-rich carrier in insoluble organic matter in carbonaceous chondrites

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Insoluble organic matter (IOM) in primitive carbonaceous chondrites is known to be enriched in deuterium, with D/H ratios > $350\times10^{-6}$. It is also characterized by a high degree of isotopic heterogeneity, as demonstrated by the observation of D-rich "hot spots" in NanoSIMS ion microprobe images (Robert *et al*. 2006). Understanding the origin of this heterogeneity represents a fundamental challenge with implications for the origin and distribution of organics in the interstellar medium and in the protoplanetary disk from which our planetary system formed.

We have determined the carrier of the isotopically anomalous hydrogen in IOM isolated from the carbonaceous chondrite Orgueil. Electron Paramagnetic Resonance spectroscopy has shown that hydrogen in the benzylic bond of organic radicals has a deuterium to hydrogen (D/H) ratio of $1.25\pm0.75\times10^{-2}$ in Orgueil IOM, which is the highest solar system D/H ratio ever reported (Delpoux *et al*. 2007).

By combining these data with quantitative image analysis recorded at a high spatial resolution with the NanoSIMS, we are able to prove that the organic radicals can account for the deuterium excess in the IOM D-rich "hot spots". Furthermore, the radicals fall on a well-defined trend between D/H ratio and C-H bond energy (Remusat *et al.* 2006), consistent with a new interpretation of the hydrogen isotopic variations in solar system organics according to which pre-existing organics exchange their D with highly deuterated gaseous molecules, such as $H_2D^+$ or $HD_2^+$. The distributions of these deuterated species is now being mapped in protostellar disks (Ceccarelli and Dominik 2005).

This conclusion runs contrary to previous interpretations, according to which the IOM is an interstellar product reprocessed in the protosolar gas and deuterium-rich "hot spot" relics of pristine interstellar organic matter, which escaped solar nebula or parent body processes.

## References

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