

Survival times of anomalous melt inclusions; Constraints from REE diffusion in olivine and chromite

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It is widely assumed that incompatible element diffusion through olivine and chromite is very slow and hence melt inclusions (MI) hosted in these minerals do not experience diffusive re-equilibration with the external magma. However, at present there are no data on diffusion coefficients for most trace elements in olivine or chromite.

We have conducted experiments at one atmosphere to determine diffusion coefficients for REE in forsteritic olivine and chromite. Clean samples of olivine and chromite that contain well-characterized MI suites were annealed with REE-doped (Pr, Ho, Tb, Lu) synthetic melts for up to 25 days at 1300-1450°C and under controlled fO_2 . Diffusion profiles were measured across sections of the crystal/synthetic melt boundary by laser-ablation ICP-MS and by electron microprobe. Element concentrations were then fitted to the diffusion equation to obtain diffusion coefficients. Calculated diffusivities for REE are relatively fast ($D = 10^{-15} \text{ m}^2/\text{s}$ at 1300°C), whereas P and Al diffusion appears to be very slow ($D < 10^{-18} \text{ m}^2/\text{s}$ at 1300°C).

MI in the olivine and chromite crystals have distinct enrichments in the REE that were doped in the external melts. The systematic degree of enrichment of Lu>Ho>Tb>Pr and correlation between degree of enrichment and MI size and/or experiment duration are all consistent with re-equilibration of these inclusions via lattice diffusion through the host crystal.

Applying our diffusion coefficients to the equations of Qin *et al.* [1], we calculate that the REE compositions of olivine- or chromite-hosted MI will completely re-equilibrate with external magma in years to decades. These timescales are consistent with the REE enrichment observed in the experimental MI, and are significantly shorter than the times estimated for magma extraction from the mantle or residence in the lower crust. Therefore, anomalous MI must be trapped in the upper crust shortly before eruption. Our results show that the assumption of chemical isolation of incompatible elements in olivine and chromite-hosted MI is not valid, and hence calls for re-evaluation of the popular interpretation that anomalous MI represent preserved samples of unmodified mantle melts.

Reference

[1] Qin Z., Lu F., Anderson Jr. A.T. (1992) *Am. Min.* **77**, 565-576.

Biogeochemical insight on the origin of carbonaceous matter in metalliferous lowest Cambrian black shale, South China

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Early Cambrian black shale deposits in the Yangtze Platform in South China are, in places, strongly enriched in Ba (~470 Mt barite and witherite), Ni, Mo, V, Co, Cr, Au, U, As, Pb, Zn, Cu, Re, and PGE. Several models have been put forward for explaining the extreme metal enrichment of the ~0.50-0.52 Ga old black shale. These include enrichment by diagenetic fluids, hydrothermal exhalation, extraterrestrial impact, synsedimentary enrichment from seawater, and discharge of petroleum into the basin. This communication presents the first results of a molecular and isotopic organic geochemical study of the metalliferous carbonaceous shale. The new biogeochemical data provide further insight into the source of the hydrocarbons and the formation of the organic matter-metal association.

The TOC content of the analysed samples is between 0.7 and 8.2 wt%. The Rock-Eval parameters were not reliable in most samples because of the low S_1 and S_2 peaks. The massive aspect of the samples without altered surfaces and coating of metal oxyhydroxides suggest indigeneity of the organic extracts. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios of the kerogen range respectively from -31.5 to -35.4‰ V-PDB and from -1.4 to 0.6‰ V-Air. The $\delta^{34}\text{S}$ values of the organic-solvent soluble molecular sulphur of black shale samples range between 13.9 and 15.8‰ V-CDT, similar to the values obtained for sulphides.

The distribution of saturated HC are characterized by: *n*-alkanes in the C_{11} - C_{31} range (maximum at C_{16} , bimodal distribution with further maxima at C_{22} or C_{26} in some samples, slight even-over-odd dominance), moderate to large *i*- C_{18} to *i*- C_{21} isoprenoid peaks, pronounced unresolved naphthenic humps in the *n*- C_{15-22} range, generally pristane and phytane in roughly equal proportion, and alkylcyclohexanes in the range C_{11} - C_{28} . Some bitumens contain C_{27} - C_{35} hopanes and C_{27} - C_{29} steranes, with the latter dominating over the former. Aromatic HC such as alkylbenzenes, naphthalene, and alkylnaphthalenes were detected only in very minor concentrations. The $\delta^{13}\text{C}$ values of *n*-alkanes and isoprenoids vary between -33 and -25‰. In all samples pristane and phytane are depleted in ^{13}C by up to 6‰ compared to C_{17} and C_{18} *n*-alkanes. All these results are best explained by derivation of hydrocarbons from algal and bacterial mats that were deposited in a saline, anoxic marine environment.