Ore deposits: An interface between the metallic and light stable isotopes

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The light stable isotopes (H, C, O, S) have proved powerful geochemical tracers of ore deposition processes in a wide variety of areas such as: geothermometry; identifying magmatic-hydrothermal and meteoric hydrothermal fluid systems; sulphide-sulphate fluid equilibria and speciation; the role of bacterial processes. In contrast, the metallic isotopes are most strongly fractionated in chemical sedimentation processes, where the transition metal elements (Fe, Cu, Mo) serve as potential tracers of both biogenic and abiogenic reduction processes and corresponding oxidation reactions. Can these two types of stable isotope system be integrated to promote the understanding of ore deposition processes? Two promising areas appear to be the combination of metallic stable isotopes with sulphur isotopes in sulphide ore mineral deposits and metallic isotopes with oxygen isotopes in oxidized ores. Studies of metal- sulphur isotope covariations are particularly suited to sedimentary ore deposition processes such as banded iron formations, stratiform sedimentary copper deposits, supergene alteration, where they can identify the involvment of bacterial processes and be used to trace redox cycles. However, use of such covariations is not limited to sedimentary processes. Low temperature continental hydrothermal processes, sea-floor hydrothermal systems and even magmatic–hydrothermal systems, may provide unique isotopic signatures. During processes such as supergene oxidation, the combination of metallic isotopes with oxygen isotopes can tell us about the evolution of the fluid-metal system.

One of the potentially important fields for the application of metallic isotopes is the use of speciation-isotope diagrams of the type developed by [1] for sulphur and carbon isotopes. Just as the SO_4–H_2S equilibria potentially control the isotopic composition of sulphide and sulphate minerals in hydrothermal systems, so speciation between oxidized and reduced solution complexes (e.g., Cu^{2+} and $CuCl_2^-$) or between oxy- and thio-anion complexes (e.g, MoO_4^{2-} and MoS_4^{2-}), can help understand the controls of metal isotope compositions in ore deposits.

Examples illustrating the above ideas, taken both from published and our own work, will be presented. Ultimately, the power of metal stable isotopes in ore deposit studies lies in their ability to explore metallic element cycling. Careful combination with the appropriate light stable isotopes can both enhance and refine the insights provided by metal stable isotopes.

Reference

[1] H. Ohmoto, *Econ. Geol.* **67**, 551 (1972).

OH in mantle olivine: Experiment vs. nature

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Olivine is the principal rock-forming mineral in the mantle lithologies. Its defect structure depends on conditions of crystallization or re-equilibration and thus can be used as an indicator of magmatic and metasomatic processes. Protonated defect structure of olivine, i.e. defect structure in which cation vacancies are charge-balanced by H^+ bonded to oxygen, is conventionally studied using FTIR (Fourier Transform Infra Red) spectroscopy. It has been shown experimentally that the frequency of OH^- IR absorption bands depends on a number of parameters, the most important of which have been proposed to be: $aSiO_2$, $aTiO_2$, and fO_2. Variation of these parameters may have similar effects on OH^- IR absorption, hampering interpretation of the spectroscopic results.

In order to isolate the major parameters controlling OH^- IR absorption at the conditions of the lithospheric mantle we studied olivines from mantle peridotitic xenoliths and kimberlitic phenocrysts using FTIR and EPMA. We did not observe correlation between OH^- IR absorption and TiO_2 content in olivine. Atomic proportion of H typically exceeds atomic proportion of Ti. We assume that Ti does not control the position and concentrations of H in olivine from the lithospheric mantle.

At increasing fO_2, concentration of ferric iron increases and one anticipates stabilization of hydrous defects associated with Fe^{3+} (lower frequency OH^- IR absorption). However, spectra indicative of OH^- associated with Me^{3+} were measured in olivines from contrasting fO_2 environments: spinel peridotites, relatively reduced diamondiferous garnet peridotites, as well as kimberlitic pheno- and xenocrysts. Thus at relatively oxidized conditions of the lithospheric mantle fO_2 does not significantly affect OH^- occurrence in mantle olivine. At the same time reduced conditions of the adiabatic upper mantle may cause preferential stabilization of the hydrogarnet-type defects (higher frequency OH^- IR absorption) rather than defects associated with Me^{3+}. Hydrogarnet-type defects are significantly more capable of storing OH^-. In that case oxidation of mantle material at the asthenosphere can cause partial dehydrogenation of olivine and thus assist melting.

We propose that the primary factor controlling OH^- solubility in olivine at conditions of the lithospheric mantle is $aSiO_2$. Peridotitic olivine in equilibrium with orthopyroxene (high $aSiO_2$) should show lower frequency OH^- IR absorption bands. However many olivine samples from mantle xenoliths show higher frequency OH^- IR absorption bands suggesting that these samples are not in equilibrium with orthopyroxene. This implies that a significant proportion of available mantle material may have been modified by transporting melts and/or metasomatic fluids, which were characterized by lower silica activities.