Post-entrapment changes to H_2O and CO_2 in olivine-hosted melt inclusions

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Olivine-hosted melt inclusions are an important source of data on magmatic volatiles. The strength of the olivine protects inclusions from decompression and degassing during ascent and eruption, preserving pre-eruptive volatiles. However, inferring mantle volatiles requires that melt inclusions remain closed systems from the time of entrapment. We used a combination of experiments and modelling to investigate the potential for post-entrapment modification of H_2O and CO_2. Our results demonstrate that proton diffusion re-equilibrates H_2O in a matter of hours, but that a significant flux of C through the host olivine is unlikely. However, H_2O changes can affect CO_2 through the formation of vapor bubbles within the inclusion. The combination of diffusive re-equilibration and vapor bubble formation significantly affect degassing paths and entrapment pressures inferred from the volatile content of melt inclusions.

Effects of diffusive re-equilibration were assessed using hydration and dehydration experiments performed on natural inclusion-bearing olivines. All run products were analyzed for major elements by electron microprobe and for H_2O and D/H ratio by SIMS. The oxidation state of Fe was determined by μ-XANES. Our results demonstrate that proton diffusion is extremely efficient at modifying the concentration of H_2O in melt inclusions. These changes do not affect the fugacity of oxygen within the inclusion, which is controlled by the creation or destruction of metal vacancies that diffuse through the olivine at rates comparable to protons.

Initially vapor-saturated inclusions are driven toward undersaturation by the loss of H_2O, so that the concentration of CO_2 is not significantly effected. This produces melt inclusions with variable CO_2 at constant H_2O, resulting in an apparent open-system degassing path. Conversely, the addition of H_2O to melt inclusions, as during magma mixing, drives inclusions toward vapor oversaturation, leading to the production of CO_2-rich vapor bubbles. Therefore, the addition of H_2O will cause melt inclusions to evolve along an isobaric CO_2 degassing path, leading to significant changes in both H_2O and CO_2.

Causes and consequences of Zn, Fe and S isotope fractionation in a large hydrothermal system: The Navan orebody, Ireland

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This study investigates the extent, causes and consequences of Zn and Fe isotope fractionation within the world-class Irish-type Navan Zn-Pb orebody, Ireland. Layered sphalerite (ZnS) has been targeted for isotopic analyses. Using samples of growth-layered sphalerite, as well as bulk Zn ore concentrates and potential source rocks, we are able to examine processes of fractionation ranging from millimeter to kilometer scales.

Large variations in δ^{66}Zn (of 0.55‰), δ^{56}Fe (of 2‰) and δ^{34}S (of 28‰) have been measured in microdrilled sphalerite. Significantly, the range of δ^{66}Zn (0.33‰) and δ^{56}Fe (0.95‰) across 3 mm of sphalerite colloform growth banding represents a substantial fraction of the range exhibited by common terrestrial rocks. Moreover, δ^{66}Zn and δ^{56}Fe display a well-defined positive correlation and both also correlate with δ^{34}S; S isotope compositions have previously been proven to monitor the extent of mixing between shallow, metal-poor, surface brines and deep, metal-rich, hydrothermal fluids in Irish-type deposits. The observed relationships represent the interplay between kinetic Zn and Fe isotope fractionation during sphalerite precipitation, and mixing of S between hydrothermal fluids and bacteriogenic brines.

Concentrate data clearly show that relatively high δ^{56}Fe and δ^{66}Zn dominate the overall system, and that lower δ^{56}Fe and δ^{66}Zn found associated with hydrothermal sulphide are a minor component of the overall deposit signature. Basement rock δ^{66}Zn data confirm that the basement is isotopically not homogenous, nor homogenised in the hydrothermal system.

Our data suggest that incoming pulses of metal-rich hydrothermal fluid triggered sulphide mineralisation, and that rapid precipitation of sphalerite from hydrothermal fluids will strongly fractionate Zn and Fe isotopes at very short time and length scales, thereby limiting the use of Fe and Zn isotopes as exploration tools. However, Zn and Fe isotopes in sulphides appear to be powerful tools to assess and decipher the physical and chemical processes responsible for the genesis of ore bodies.