SIMS sensitivity factors of ^{2}H and $^{16}O^{2}H$ relative to ^{18}O in spinel-structured oxides

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Spinel-structured oxides ("spinels") are a group of nominally anhydrous minerals characterized by a wide range of solid solution. To allow the analysis of hydrogen in spinels by ion microprobe, Relative Sensitivity Factors (RSFs), which are typically matrix-dependent, need to be determined. For this work, we have selected five natural spinels from the Mg-Al-Fe-Ti-Cr-Mn-Zn compositional space. We present an approach to estimate spinel density on basis of bulk chemical composition determined by electron microprobe. Densities in our samples range from 3.7 to 5.1 g cm^{-3}. Samples were implanted with a fixed dose of deuterium (1 x 10^{15} atoms cm^{-2}) using an ion energy of 40 keV. Subsequently, we performed depth profiling using a Cs^{+} primary beam on the Cameca ims-1270 ion microprobe at Hokkaido University, monitoring secondary ion counts of ^{2}H and ^{18}O, and at high mass-resolution $^{16}O^{2}H$, $^{17}O^{1}H$, and ^{18}O, until the implanted ion counts dropped below background levels. From the reduced data, we calculated the RSFs for secondary ions of atomic ^{2}H and molecular $^{16}O^{2}H$ relative to ^{18}O as matrix element. RSFs for ^{2}H are similar for all spinels at 1.11 ±0.32 (2 σ) x 10^{22} atoms cm^{-3}, indicating a small matrix effect for ^{2}H despite the large compositional range of spinels studied. In contrast, RSFs for $^{16}O^{2}H$ relative to ^{18}O decrease with spinel density from 2.65 ±0.36 (2 σ) x 10^{21} atoms cm^{-3} at 3.7 g cm^{-3} to 3.41 ±0.73 (2 σ) x 10^{20} atoms cm^{-3} at > 4.5 g cm^{-3}, indicating a strong matrix effect on secondary dimer production during processes of ion sputtering and secondary ionization. Our data imply that the analysis of water in natural spinels may be undertaken through measurement of H or OH, but that spinel densities must be well-determined in the case of OH measurement. Mineral density effects on RSF values will have to be evaluated prior to analysis of water in other nominally anhydrous solid solution minerals.

Keywords: spinel-structured oxides, relative sensitivity factors, secondary ion mass spectrometry, hydrogen analysis, nominally anhydrous minerals

