# FTIR spectrum of OH in olivine: A new tool in diamond exploration

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FTIR spectroscopy revealed anomalously high hydroxyl concentrations in kimberlitic olivines from South Africa and Siberia. The purpose of our current study is to test whether this finding merely represents an anomaly or whether kimberlitic olivines from other cratonic areas, including Canada, are also high in hydroxyl content. In the latter case such a distinct FTIR signature could be used to discriminate between kimberlitic and non-kimberlitic olivines in exploration till samples collected in the Canadian Arctic.

We measured FTIR spectra and chemical compositions of olivines from seven Canadian kimberlites. Single-grain FTIR measurements were performed in transmittance mode on double polished, ~300 micron thick sections of individual olivines and rock slabs. For application in diamond exploration the method was also tested on unpolished samples.

The majority of olivines exhibit strong OH-related IR absorption bands in the wavenumber range from 3670 to 3230cm$^{-1}$. A large proportion of olivines predominantly absorb at higher frequencies in the wavenumber range from 3670 to 3440 cm$^{-1}$ (Group 1 OH bands). Noteworthy are high frequency IR peaks at wavenumbers >3570 cm$^{-1}$, that are common for olivines originating at high pressures but that are not observed in spectra of basaltic phenocrysts. Some olivines also show absorption at lower frequencies between 3240 and 3340 cm$^{-1}$ (Group 2 OH bands). Group 2 OH bands indicate equilibrium with orthopyroxene and thus may reflect a peridotitic origin of olivine macrocrysts in kimberlites. Hydroxyl concentrations vary from grain to grain but typically remain constant across individual grains. So far, we have observed no correlation between the frequency or intensity of absorption bands and the trace element composition of olivines. A significant proportion of the studied kimberlitic olivines show OH concentrations that are not only much higher than those reported for olivines crystallized at lower water fugacities (mantle xenoliths) but also than those of olivines formed under hydrous conditions but at shallower depth (e.g. phenocrysts from boninites; Matveev et al., 2005). Spectra measured on unpolished grains exhibit broader absorption bands and higher spectral noise, but otherwise are sufficiently similar to spectra of polished samples to suggest that FTIR spectroscopy can be used to identify kimberlitic olivines even with unpolished grains.

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# Hydration of olivine and the Earth's deep water cycle

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Although natural olivine of upper mantle origin generally contains less than 300 ppm $H_2O$ by weight, olivine synthesized at temperature and pressure conditions near the 410 km discontinuity, can contain up to 20 times this amount of H, enough to affect elastic properties, crystal structures, and unit cell volumes. Hydrous olivines have been synthesized at 12 GPa and several temperatures and bulk compositions to examine the effects of silica activity, and temperature on H contents of the olivine. Mineral phases were identified by Raman spectroscopy and analyzed for H content by FTIR spectroscopy of oriented, faceted grains.

$Fo_{95}$ olivines synthesized at 1250°C have been observed with up to 5000 ppm $H_2O$ coexisting with clinoenstatite and up to 8000 ppm $H_2O$ coexisting with clinohumite. Pure-Mg forsterites synthesized at 1250° have been observed with up to 8000 ppm $H_2O$ coexisting with clinoenstatite and 8500 ppm $H_2O$ coexisting with clinohumite.

Crystal structure refinements indicate that the hydration mechanisms are different in the two different conditions. The silica-excess sample appears to contain M2 cation vacancies, whereas the magnesia-excess sample shows tetrahedral site vacancies up to two percent, consistent with 5000 ppm by weight $H_2O$. Further, the partially vacant coordination polyhedra are significantly larger than their fully occupied counterparts. Cell parameter refinements indicate expansion of the unit cell by up to 0.3 percent with hydration in both samples, with tetrahedral vacancies causing an increase in both *b* and *c* axes and contraction of *a* relative to the crystal showing octahedral vacancies. Static compression measurements by single crystal X-ray diffraction to 8GPa indicate a decrease in the bulk modulus from about 129GPa for anhydrous forsterite to 120 GPa for a sample containing 8000 ppm $H_2O$.

These results indicate that olivine can be a major host for H at depths greater than 200 km in the mantle. If olivine can contain these relatively high H contents, it is unlikely that major melting would occur at 410 km in a mantle containing a two thousand ppm $H_2O$ in a region of ascending convection.