# OH/F local environment in metamict titanite by $^1$H and $^{19}$F MAS NMR spectroscopy

J. M. WENNEKAMP[1], M. FECHTELKORD[1] AND L.A. GROAT[2]

[1]Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität-Bochum, Universitätsstraße 150, 44780 Bochum, Germany (Johannes.Wennekamp@ruhr-uni-bochum.de)

[2]Department of Earth and Ocean Sciences, The University of British Columbia, 6339 Stores Road, Vancouver, BC, V6T 1Z4, Canada

Titanite is a common accessory mineral in igneous and metamorphic rocks. The ideal formula is $CaTi(SiO_4)O$, but there can be extensive substitution at both cation and anion sites. Calcium may be replaced by Na, REEs, Y, U, and Th. To maintain electroneutrality there are also substitutions at the site of the (O) anion that is not bonded to Si. Thus $(OH)^-$ and F can replace $O^{2-}$ in significant amounts, coupling with the cation substitutions to satisfy the overall constraint of electroneutrality. The radionuclides U and Th are responsible for alpha-decay events which mainly result in atomic displacements which cause increasing damage to the crystalline structure (metamictization; Ewing *et al.* 1987). The study of metamictization could help to find nuclear waste deposits since the metamicts have experienced a long-term damage by radionuclide decays.

We have examined a series of chemically and structurally well-characterized titanite samples by $^1$H and $^{19}$F MAS NMR spectroscopy to investigate the local structural environment of OH and F inside the structure as a function of the tructural distortion caused by metamictization. Titanite samples with a varying degree of alpha-decay damage were selected for the experimental study. Most of the samples are from Norway and they have previously been characterized using IR spectroscopy, electron microprobe, powder X-ray diffraction, HRTEM, EXAFS-XANES spectroscopy and $^{29}$Si MAS NMR spectroscopy (Hawthorne *et al.* 1991).

Our preliminary results show that the amount of OH increases with the degree of alpha-decay damage. Both $^{19}$F and $^1$H MAS NMR show that the increasing amorphization results in significant NMR line broadening.

## References

Ewing R.C., Chakoumakos B.C., Lumpkin G.R., and Murakami T., (1987), *MRS Bulletin* **MAY/JUNE,** 59-66.

Hawthorne F.C., Groat L.A., Raudsepp M., Ball N.A., Kimata M., Spike F.D., Gaba R., Halden N.M., Lumpkin G.R., Ewing R.C., Greegor R.B., Lytle F.W., Ercit T.S., Rossman G.R., Wicks F.J., Ramik R.A., Sherriff B.L., Fleet M.E. and McCammon C., (1991), *American Mineralogist* **76**, 370-396.

# Spin transition in magnesiowüstite in Earth's lower mantle

R.M.M. WENTZCOVITCH

Minnesota Supercomputing Institute and Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Ave SE, Minneapolis MN 55455, USA (wentzcov@cems.umn.edu)

Iron in the major lower mantle (LM) minerals undergoes a high spin (HS) to low spin (LS) transition at relevant pressures (23–135 GPa). Previous failures of standard first principles approaches to describe this phenomenon have hindered its investigation and the clarification of important consequences. Using a rotationally invariant formulation of LDA+$U$ we report a successful study of this transition in low solute concentration magnesiowüstite, $Mg_xFe_xO$, ($x$< 0.2), the second most abundant LM phase. We show that the HS-LS transition goes through an insulating (semiconducting) intermediate mixed spins (MS) state without discontinuous changes in properties, as seen experimentally. We show that the HS state crosses over smoothly to the LS state passing through an insulating MS state where properties change continuously. We address the change in elastic properties across this transition and its significance for the interpretation of seismic data.

Work done in collatoration with T. Tsuchiya , C. R. S. da Silva, and J. F. Justo F., and Z. Wu. Research supported by NSF/EAR 013533, 0230319, 0635990, and NSF/ITR 0428774 (*VLab*).