Failure of density functional theory for ground state calculations on TiO_2

GERD STEINLE-NEUMANN[1], VOJTECH VLČEK[1], EVA HOLBIG[1] AND XIANG WU[1,2]

[1]Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany
[2]School of Earth and Space Sciences, Peking University, Beijing 100871, China

Electronic structure computations based on density functional theory (DFT) is playing an increasingly important role in the study of material properties, including high pressure properties that are relevant for Earth's interior. The success of DFT-based computations has been limited by the failure of standard implementations of DFT to properly describe the transtion metal-bearing oxides and silicates that are of great importance in the Earth's mantle, especially for Fe-bearing compounds.

There is less appreciation of DFT failures for lighter transition metal-bearing materials. For SiO_2 it is documented that with the local density approximation (LDA) stishovite is predicted stable over quartz which is corrected by the introduction of the generalized gradient approximation (GGA) [1]. However, experimental structural parameters and physical properties of quartz are better reproduced by LDA [1]. Similarly, and not well documented, for TiO_2 DFT in any approximation predicts rutile stable over anatase, in conflict with calorimetry [2].

We have revisited the relative stability of TiO_2 anatase and rutile, as well as other crystalline phases, with highly accurate all-electron methods and various approximations to exchange and correlation, and confirm that rutile is always found stable over anatase. Also, computing harmonic zero point motion energy for the two phases from linear response phonon computations does not stabilize anatase. However, a strong anharmonic character of rutile lattice vibration is revealed that warrants further studies.

High pressure phase relations are better reproduced within DFT, and a proper sequence of high pressure phase stability is reproduced [3]. Zero pressure bulk moduli are all below 240 GPa, sugessting that there are no superhard phases of TiO_2. Higher coordination of high pressure phase leads to stronger localization of the Ti 3d states.

[1] Haman (1996) *Phys. Rev. Lett.* **76**, 660. [2] Ranade *et al.* (2002) *Proc. National Academy of Sciences* **99**, 6476. [3] Wu *et al.* (2010) *J. Phys. Cond. Matter* **22**, 295501.

Detection of airborne radionuclides released during the nuclear accident at Fukushima Daiichi over Europe

P. STEINMANN[1]*, O. MASSON[2], R. GURRIARAN3, H. WERSHOFEN[4] AND RO5 COMMUNITY MEMBERS[5]

[1]Federal Office of Public Health, 3003 Bern, Switzerland (*correspondence: philipp.steinmann@bag.admin.ch)
[2]IRSN, 13115 Saint Paul lez Durance, France
[3]IRSN, 91400 Orsay, France
[4]PTB, 38116 Braunschweig, Germany
[5]"Ring of 5 (Ro5)" is an informal group dedicated to the survey of artificial radioacitvity in the atmosphere

Atmospheric release of radioactivity after the nuclear accident at Fukushima Daiichi started on the 12th of March 2011. Within approximately 10 days contaminated air masses reached Europe. The long range transport resulted in a dilution of the activity concentrations in the air by a factor on the order of 10000 times compared to concentrations reported from Japan. With levels of some tens of mBq m^{-3} at the most, there has been no health safety risk in Europe. The dispersion of the radioactive traces over Europe were followed through the analyses of filters of more than 140 high-volume samplers. Rapid exchange of data was granted through the participation of many laboratories in a network called "Ring of Five (Ro5)" which is an informal information club started in 1983 for this very purpose.

Switzerland was situated at the edge of a corridor with higher levels and saw comparatively low maximum total ^{131}I activities of around 2 mBq m^{-3}. At the end of March the activity ratios of gaseous ^{131}I/particulate ^{131}I recorded in Switzerland were around 4 to 6, while the activity ratio of particulate $^{131}I/^{137}Cs$ was roughly 10. Samples taken with airplanes in the upper troposphere as well as samples from a high altitude station at Jungfraujoch (3500 m a.s.l.) allowed to assess the vertical mixing of the radioactive traces. Temporal evolution of isotopic ratios such as $^{132}Te/^{137}Cs$ or $^{136}Cs/^{137}Cs$ helped to estimate the duration of the major emissions as well as the composition of the source term.

In Switzerland atmospheric deposition of radioactivity was very low with only a few Bq m^{-2} for ^{131}I. This lead to spurious contamination of grass and leafy vegetables (up to a few Bq kg^{-1} fresh weight). Again, at these levels there has been no food safety risk.