

Raman scattering, terrestrial ringwoodite and beyond...

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The National Science Day is celebrated in India on 28 February each year to mark the discovery of the Raman effect. The striking scientific discovery of the Raman effect was announced in 1928 at a scientific meeting in Bangalore, where Raman concluded, 'We are obviously only at the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and wave theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics, and chemistry. It all remains to be worked out.' For this outstanding fundamental contribution, two years later, Raman was awarded with the Nobel Prize in Physics in 1930 and the concluding remark made by him during the 1928 meeting started to become reality with the advent of laser source. Today Raman scattering has found a wide variety of applications in different areas of science and technology that include: (i) physics, chemistry and materials science, (ii) geology, petrochemistry and polymers, (iii) biological science, (iv) pharmaceutical industry, (v) nuclear science, (vi) forensic science, etc.

As we just conclude our National Science Day celebrations this year, Pearson *et al.*¹ (University of Alberta, Canada) have made a landmark study using Raman scattering to reveal the presence of a high-pressure form of mineral oli-

vine [(Mg,Fe)₂SiO₄], called the 'ringwoodite'. The sample used in the study was an impure tiny diamond ~5 mm long (Figure 1) from the Juína district of Brazil. Pearson *et al.*¹ used Raman spectroscopy to examine the impurities included within the Juína diamond, and came across a 40 µm grain of ringwoodite within it. They also used the shift in Raman band in the diamond to estimate the trapped high pressure next to the ringwoodite, indicating that the mineral was trapped inside the diamond and resided in its original compressed form. Further examination using infrared spectroscopy on the tiny ringwoodite grain revealed that it contained ~1% water by weight.

What makes the discovery significant?

The region of the mantle that separates the upper and lower mantle is known as the mantle transition zone (MTZ), which is bounded by well-resolved seismic discontinuities at 410 and 660 km depths. While the 410 km discontinuity is mineralogically characterized by phase transition of olivine (from α -olivine to β -olivine or wadsleyite), the 660 km seismic discontinuity is a result of dissociation of γ -phase of olivine (ringwoodite) to perovskite and wüstite². The impact of the study by Pearson *et al.*¹ is that

although the minerals wadsleyite and ringwoodite are considered to make up most of the 250 km thick MTZ, the presence of ringwoodite was hitherto unconfirmed via actual sampling. Previous studies reported its presence either in meteorites³ or they were synthesized in the laboratory⁴⁻⁶. This new discovery of natural terrestrial ringwoodite assumes significance as it opens up a large number of long-standing issues related to the planet Earth. For example, (i) if such wet pockets are distributed within the mantle, what is the nature of their distribution? (ii) Are they capable of inducing material flow and convection differently? (iii) If so, what is the timescale? (iv) How much water is present within MTZ, particularly in view of its ability to hold substantial amounts of water⁷⁻⁹. (v) The origin of terrestrial water^{10,11} and its recycling within the planet Earth (i.e. Earth's primordial water versus recycled water via subducted oceanic crust). (vi) Effect of water-bearing pockets on the nature of seismic discontinuities at MTZ¹². (vii) Hydrous MTZ and its role on terrestrial magmatism and plate tectonics¹³⁻¹⁵. (viii) The role of wet pockets in MTZ vis-à-vis observed discrepancies between the seismological and mineralogical Claypeyron slopes.

Based on our recent study¹⁶, the last point mentioned above needs further elaboration. While evaluating the depth of mantle plumes using P-to-S converted seismic waves from the 410 and 660 km depth discontinuities, we studied disposition of these boundaries beneath prominent oceanic hotspot regions distributed on the globe. The basic premise of our work was to register the movements of the 410 and 660 km seismic discontinuities in response to excess thermal anomalies associated with mantle plumes. The idea was that if the plumes originate in the lower mantle, the thickness of MTZs near the hotspot location should shrink. This is because the transition of α - to β -phase of olivine bears a positive dP/dT (ref. 17) resulting in downward movement of the 410 km seismic boundary, whereas breakdown of γ -olivine to perovskite and wüstite with negative dP/dT (ref. 18) would cause upward



Figure 1. Enlarged image of impure diamond from Juína, Brazil (courtesy: Graham Pearson, University of Alberta). The diamond is 5 mm in long axis. A microscopic inclusion of ringwoodite, which is a high-pressure polymorph of mineral olivine [(Mg,Fe)₂SiO₄] was documented using Raman spectroscopy by Pearson *et al.*¹.

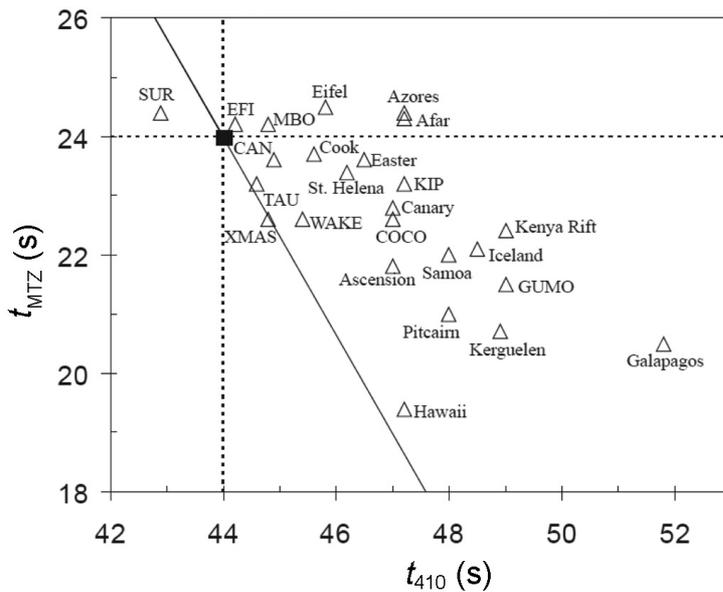


Figure 2. The t_{MTZ} times (P660s–P410s) as a function of Ps conversion times from the 410 km discontinuity (t_{410}). Hotspots are plotted with their names whereas locations away from hotspots are plotted by their station codes (for details see ref. 16). Filled black square corresponds to the IASP91 reference model¹⁹.

movement of the 660 km discontinuity. Therefore, the extent of shrinkage of MTZ is dictated by the thermal anomaly associated with the plume under consideration. We found that a large number of oceanic hotspots as well as some continental hotspots indeed have their origin in the transition zone or deeper. As a corollary to this study we also attempted to integrate our seismological findings with effective mineralogical Clapeyron slope. However, we found in the plot between differential arrival times of P660s and P410s (i.e. $t_{\text{MTZ}} = \text{P660s} - \text{P410s}$) and Ps conversion times from the 410 km discontinuity (t_{410}) that the points do not strictly adhere to the expected Clapeyron slope line and deviate to the right of the expected mineralogical trend (Figure 2). At most of the hotspot locations (stations), this deviation can be due to an extremely slow mantle above the 410 km boundary. The most plausible explanation for the observed deviation from the

expected mineralogical trend may now be attributed either due to wet pockets within the MTZ as documented in Pearson *et al.*¹, or due to possible presence of upper mantle heterogeneities beneath each station, or both. The discovery by Pearson *et al.*¹ will certainly pave the way to fresh insights and open up challenging frontier researches in the field of earth system science.

1. Pearson, D. G. *et al.*, *Nature*, 2014, **507**, 221–224.
2. Helffrich, G. R. and Wood, B. J., *Nature*, 2001, **412**, 501–507.
3. Binns, R., Davis, R. J. and Reed, S. J. B., *Nature*, 1969, **221**, 943–944.
4. Chen, J., Inoue, T., Yurimoto, H. and Weidner, D. J., *Geophys. Res. Lett.*, 2002, **29**, 1875.
5. Kohlstedt, D. L., Keppler, H., and Rubie, D. C., *Contrib. Mineral. Petrol.*, 1996, **123**, 345–357.
6. Smyth, J. R., Holl, C. R., Frost, D. J., Jacobsen, S. D., Langenhorst, F. and

McCammon, C. A., *Am. Mineral.*, 2003, **88**, 1402–1407.

7. Miller, G. H., Rossman, G. R. and Harlow, G., *Phys. Chem. Minerals*, 1987, **14**, 461–472.
8. Bell, D. R. and Rossman, G. R., *Science*, 1992, **255**, 1391–1397.
9. Berry, A. J., Hermann, J., O'Neill, H. S. C. and Foran, G. J., *Geology*, 2005, **33**, 869–872.
10. Drake, M. J., *Meteoritics Planet. Sci.*, 2005, **40**, 1–9.
11. Ciesla, F. J., Lauretta, D. S. and Hood, L. L., In 35th Lunar and Planetary Science Conference (abstr. #1219), Houston, Texas, USA, 2004.
12. Wood, B. J., *Science*, 1995, **268**, 74–76.
13. Bercovici, D. and Karato, S., *Nature*, 2003, **425**, 39–44.
14. Bolfan-Casanova, N., *Mineral. Mag.*, 2005, **69**, 229–258.
15. Hirschmann, M., *Annu. Rev. Earth Planet. Sci.*, 2006, **34**, 629–653.
16. Das Sharma, S., Ramesh, D. S., Li, X., Yuan, X., Sreenivas, B. and Kind, R., *Geophys. J. Int.*, 2010, **180**, 49–58.
17. Katsura, T. and Ito, E., *J. Geophys. Res.*, 1989, **94**, 15663–15670.
18. Akaogi, M., Ito, E. and Navrotsky, A., *J. Geophys. Res.*, 1989, **94**, 15671–15685.
19. Kennett, B. L. N. and Engdhal, E. R., *Geophys. J. Intl.*, 1991, **105**, 429–466.

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