New Insights Into The Zircon-Reidite Phase Transition As An Indicator Of Impact Structures. C. Stangarone[1], R. J. Angel[2], M. Prencipe[3], B. Mihailova[4], M. Alvaro[2] and Joern Helbert[1], [1]Institute for Planetary Research, Deutschen Zentrums für Luft- und Raumfahrt, Berlin, Germany (claudia.stangarone@dlr.de), [2] Department of Earth and Environmental Sciences, University of Pavia, Via A. Ferrata, 1 I-27100, Pavia, Italy, [3] Earth Sciences Department, University of Torino, Via Valperga Caluso 35 Italy, [4] Department of Earth Sciences, University of Hamburg, Grindelallee 48, D-20146 Hamburg, Germany

Introduction: Upon meteorite bombardment zircon ($ZrSiO_4$) starts showing shock microstructures at or above 20 GPa [1]. These microstructures survive subsequent metamorphism without being obliterated, thus they can provide diagnostic criteria to identify impact structures [2]. During shocks zircon may also transform into the high-pressure scheelite-type polymorph reidite [3]. Therefore, studying the stability relationships between zircon and its high-pressure polymorph reidite may be crucial to constrain the impact conditions of an impact structure. However, the experimental data on the high-pressure phase relations are rather unclear. Shock wave studies found this transformation to occur at high pressures (30–50 GPa) [4], [5] and at microsecond time scales supporting a martensitic transformation mechanism for impact-produced reidite [6]. However topological differences and thermodynamics, supported by DFT calculations [7], suggest that the phase transition is reconstructive. Nonetheless, the equilibrium transition pressure, investigated with static loading experiments, is not well constrained, with reidite occurrences at much lower pressure and ranging from 8 up to 23 GPa [8], [9].

Methods: To resolve the ambiguities in the experimental data we have performed HF/DFT calculations of zircon and reidite to determine their structures, elastic behavior, phonon frequencies and the energy curves as a function of pressure (up to 25 GPa and 17 GPa respectively) at 0 K. We also provide calculated Raman spectra which will aid in the identification of the polymorphs of zircon, in comparisons with experimental evidences [10].

Results: DFT calculations revealed that the softening of a silent (B_{1u}) mode of zircon leads to a phase transition to a "*high-pressure-low-symmetry*" (HPLS) $ZrSiO_4$ polymorph with space group and cell parameters a=6.4512 Å c=5.9121Å V = 246.05Å3 (at 20 GPa). The primary coordination of SiO_4 and ZrO_8 groups in the structure of zircon is maintained in the high-pressure phase, and the new phase deviates from that of zircon by the rotation of SiO_4 tetrahedra and small distortions of the ZrO_8 dodecahedra. The new polymorph is stable with respect to zircon at 20 GPa and remains a dynamically-stable structure up to at least 30 GPa. On pressure release the new phase reverts back to the zircon structure, and therefore cannot be quenched in experiments. In contrast, the transformation from zircon to reidite is reconstructive in nature and results in a first-order transition with a volume and density change of about 9%. The calculated energies from the DFT simulations yield an equilibrium transition pressure of 9.13(1) GPa at 0 K. Simulations of the Raman spectra of the three polymorphs at 20 GPa show how they can be distinguished. In particular, the peak due to the lowest-energy A_1 mode with a calculated wavenumber of 94 cm^{-1} is diagnostic of the HPLS phase because it does not overlap with any of the peaks of zircon or reidite (Figure 1).

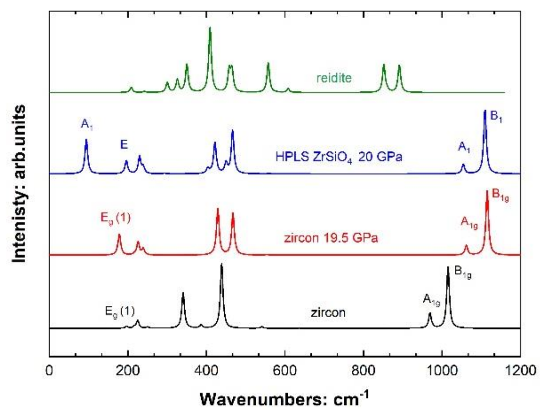

Figure 1: Calculated Raman spectra of the three polymorphs: the spectra are simulated for a polycrystalline powder without any polarization.

Conclusions: We have discovered that above 20 GPa zircon undergoes a displacive phase transition to a new polymorph. The discovery of this new polymorph resolves the apparent discrepancies between experimental studies reported in the literature, and allows us to clarify the phase relations of $ZrSiO_4$. We also report calculated Raman spectra for all three polymorphs and provide specific guidelines for distinguishing the three polymorphs in experimental Raman spectra. New Raman scattering experiments confirm the occurrence of a soft-mode-driven zircon-to-HPLS phase transition at ~21 GPa [10].

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References: [1] Leroux H. et al. (1999) *EPSL*, 169, 291–301. [2] Reddy S.M. et al. (2015) *Geology*, 43, 899–902. [3] Liu L.G. (1979) *EPSL*, 44, 390–396. [4] Kusaba K.. et al. (1986) *J. Phys. Chem. Solids*, 47, 675. [5] Gucsik A. (2004) *Mineral Mag*, 68, 801–811. [6] Langenhorst F. and Deutsch A. (2012) *Elements*, 8, 31–36. [7] Dutta, R., and Mandal, N. (2012a) *Comp Mater Sci*, 54, 157–164. [8] Ono S. et al. (2004a) *Am Min* 89, 185–188. [9] Van Westrenen W. (2004) *Am Min*, 89, 197–203. [10] Mihailova B. (2019) DGK XXVII, abstract #69.