# A COMPARISON OF MICROSTRUCTURES AMONG SOME OF THE EARLIEST-FORMED ZIRCONS

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**Introduction:** Meteoritic zircon has proven to be highly useful for unravelling the igneous, thermal-metamorphic and impact record of its host parent body (e.g., [1-3]). However, its occurrence is highly diverse among distinct meteorites groups and samples therein. Prime sources are differentiated rocks, i.e., lunar meteorites and rocks, samples of the howardite-eucrite-diogenite (HED) suite with basaltic eucrites in particular, some mesosiderites (see [4], and refs. therein), and the unique martian regolith breccia Northwest Africa (NWA) 7034 and paired samples [5,6]. In this initial comparative study we investigated the internal chemical and structural zonation patterns of zircon at high spatial resolution, relevant for chronological and petrological constraints and a first step in comparing planetary petrogenesis. The observed degree of radiation damage and occurrence/absence of chemical zoning patterns are significant for unravelling the formation conditions of their host rocks and are potentially useful to discriminate discrete chemical and physical processes characteristic of their parent body.

**Material and Methods:** We have used a series of non-destructive, spatially high-resolution techniques for a detailed structural and chemical characterization of individual zircon grains derived from large differentiated asteroids, Mars and the early Earth. Analytical techniques include electron microscopy-based investigations (SEM-CL, EPMA and EBSD), Raman spectroscopy and photoluminescence. The sample set includes the martian regolith breccias NWA 7906 and NWA 7475, paired with NWA 7034 [5,6], and the basaltic eucrites Camel Donga, Cachari, Dhofar 182, Hammadah al Hamra (HaH) 286, Jonzac, NWA 1000, NWA 4523, representing a wide range of shock- and thermal metamorphic conditions, and which are compared to one of the oldest known (detrital) terrestrial zircon grains from the Jack Hills in Western Australia, which hosts a Hadean-aged core [7].

**Results:** In the eucrite sample suite, the occurrence of igneous zoning features such as planar growth banding and sector zoning is poorest and commonly modified by widespread thermal metamorphism to produce rounded, sub- to anhedral zircon grains sometimes forming metamorphic rims and polycrystalline aggregates. In HaH 286 a unique ~80 µm skeletal-shaped zircon assemblage composed of ~5 µm individual grains intergrown with ilmenite is observed. In contrast, the martian regolith breccia contain sub- to anhedral zircon crystals (5-40 µm) occurring in evolved igneous clasts and in the silicate matrix (in agreement with [6]) with preserved igneous zonation, i.e., planar and concentric growth bands. Raman spectroscopic data show a moderate- to strong structural disorder for most grains in both eucrite and martian samples. Broadening and red-shifting of the monitored prominent, anti-symmetric $\nu_3(SiO_4)$ stretching band (i.e., located at ~1008 $cm^{-1}$ in undamaged zircon) indicate radiation damage assigned to the alpha decay of trace actinides. The EBSD data quality, i.e., the diffraction signal strength, is spatially correlated with the crystallinity shown by CL and Raman data, indicating the survival of the pre-launch generated structural and chemical zoning of extraterrestrial zircon grains.

**Discussion:** Some of the investigated grains share common igneous features such as planar growth banding, sector zoning, i.e., textures similar to that of terrestrial high-temperature zircon, preserved since their formation. Zoning and chemical microstructure of asteroidal zircon grains, however, appear to be the most complex as a result of thermal- and shock metamorphism, consistent with the complex petrology of the samples. Measured Raman band widths (i.e., FWHM) and corresponding shift of $\nu_3(SiO_4)$ position indicate a certain degree of radiation damage and structural recovery (i.e., annealing) observed in all zircon grains, regardless of the varying thermal-metamorphic histories. Raman data further suggest that a subset of grains in half of the eucrites and all zircon grains in both Martian meteorites show an unusual down-shift in the $\nu_3(SiO_4)$ position compared to terrestrial grains. Secondary rounding and fracturing of martian zircon can be explained by re-deposition through surface processes. Porosity on a sub-µm scale observed in some domains of martian zircon, as indicated by deficient EPMA totals, low CL- and variable Raman signals restricted to these areas are clearly not primary igneous features. The investigated terrestrial Hadean zircon grain is distinct from martian regolith and asteroidal populations with regard to its pervasive annealed fractures hosting secondary, sometimes hydrous, mineral inclusions, all of which reflect residence in a planet with a long-lived hydrosphere and more dynamic crust.

**References:** [1] Haba M. K. et al. (2014) *Earth and Planetary Science Letters* 387:10–21. [2] Roszjar J. et al. (2016) *Earth and Planetary Science Letters* 452:216–226. [3] Nemchin A.A. et al. (2014) *Nature Geoscience* 7:638–642. [4] Roszjar J. et al. (2014) *Chemie der Erde-Geochemistry* 74:453–469. [5] Agee C. B. et al. (2013) *Science* 339:780–785. [6] Humayun M. et al. (2013) *Nature* 503:513–516. [7] Valley J. W. et al. (2014) *Nature Geoscience* 7:219–223.