

Evaluating the serpentinization degree of Martian analogues through the RLS ExoMars simulator: univariate semi-quantification method

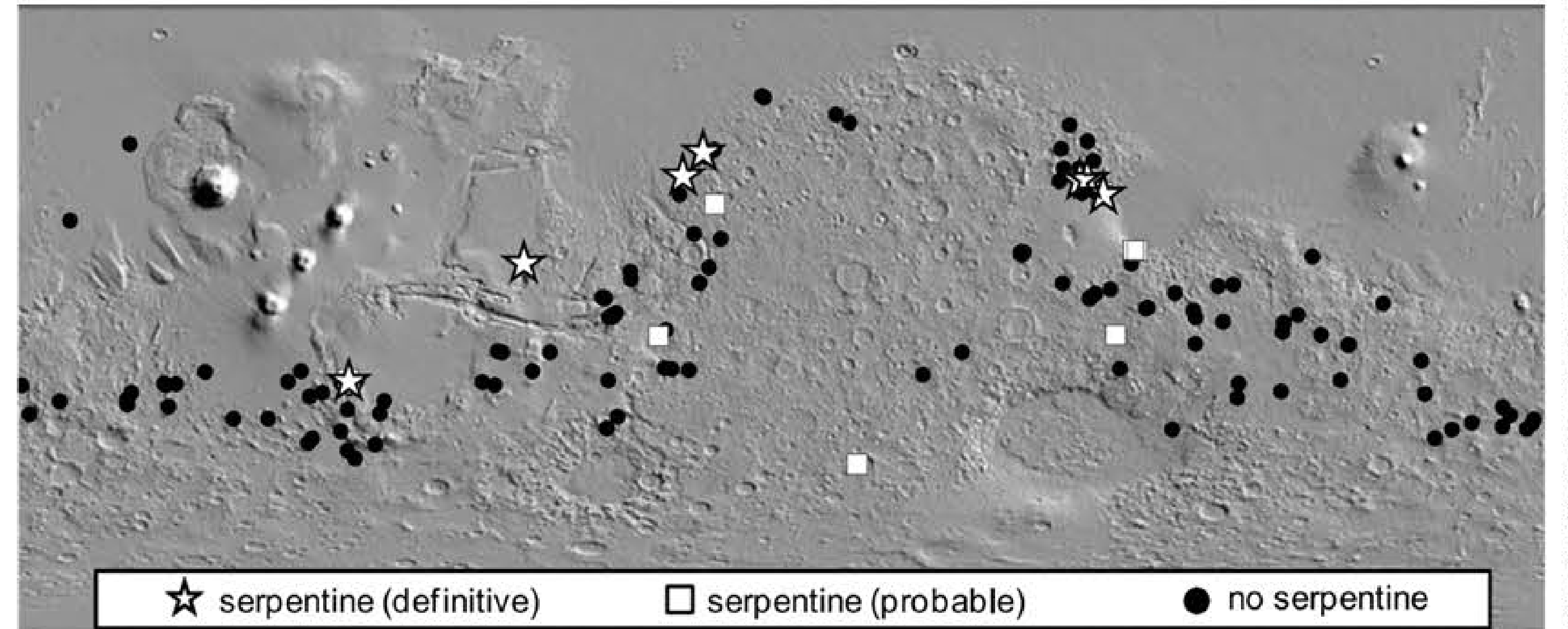
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Serpentinized olivine on Mars: a priority astrobiological scientific target

Picritic basalts have been detected at Jezero Crater and Oxia Planum, the landing sites of the Mars2020 and ExoMars rover missions. The analytical characterization of olivine grains and their alteration products are considered a strong scientific target for astrobiological studies. Indeed, olivine can be easily serpentinized by water/rock interactions. On Earth, H_2 and CH_4 released during serpentinization fuel microorganism proliferation, which biomarkers are retained and preserved within the lamellar structure of the alteration product (serpentine). Considering that Martian rocks' serpentinization has been confirmed by orbital data, the scientific community is evaluating the potential connection between olivine alteration and life proliferation on Mars.



The Raman Laser Spectrometer (RLS) onboard the ExoMars Rover

The aim of the ExoMars rover is to find traces of life on Mars. The success of the mission will be fully entrusted to the combined use of complementary spectroscopic tools. In detail, Raman (RLS and VISNIR (MicrOmega) instruments will be crucial for the selection of potential biomarkers-bearing samples to be analyzed on-site by the Mars Organic Molecule Analyzer (MOMA).

RLS flight model (FM)

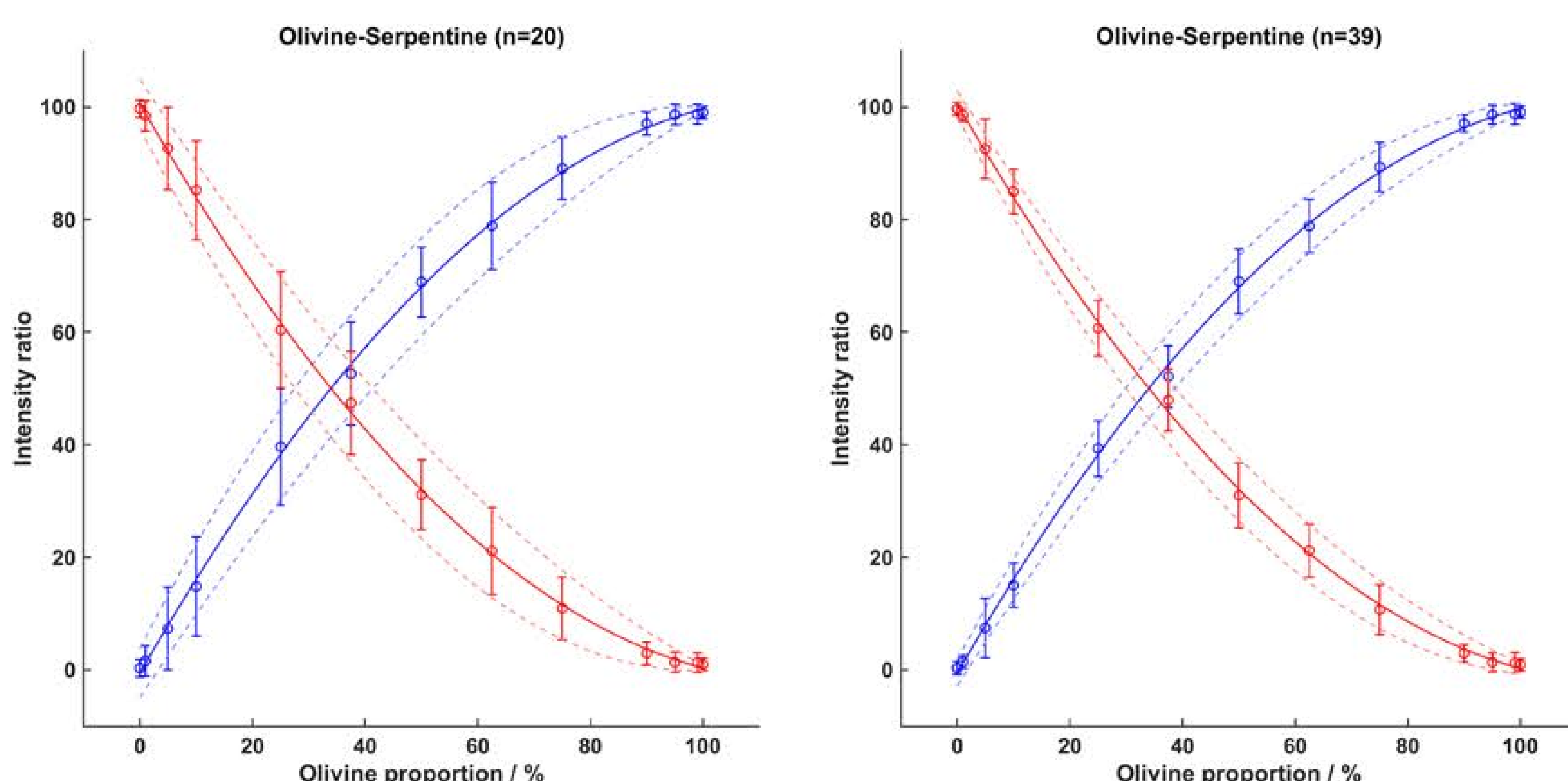
The instrument is made of three main components: the spectrometer unit (SPU), the internal optical head (iOH) and the electronics control unit (ICEU). The ICEU is composed of three electronic boards and contains a Nd:YAG diode laser emitting at 532 nm. The iOH unit focuses the excitation laser into the samples and collects Raman scattering (200-3800 cm^{-1}). At the SPU, the Raman signal is collimated, diffracted and focused onto the CCD detector. RLS will be used to collect between 20 and 39 spectra from each powdered Martian sample

RLS ExoMars Simulator

This is considered the most reliable tool to effectively simulate the automatic operational mode of the RLS FM and is used to reliably predict its potential scientific outcome. Range of analysis (70-4200 cm^{-1}), working distance (≈ 15 mm), laser wavelength (532 nm), spectral resolution (6-10 cm^{-1}) and spot of analysis ($\approx 50 \mu m$) of this instrument resemble those of the RLS instrument. Furthermore, it integrates the same algorithms employed by the RLS to autonomously operate on Mars, such autofocus, acquisition parameters optimization etc.

RLS semi-quantification of the olivine/serpentine ratio of Martian analogue materials

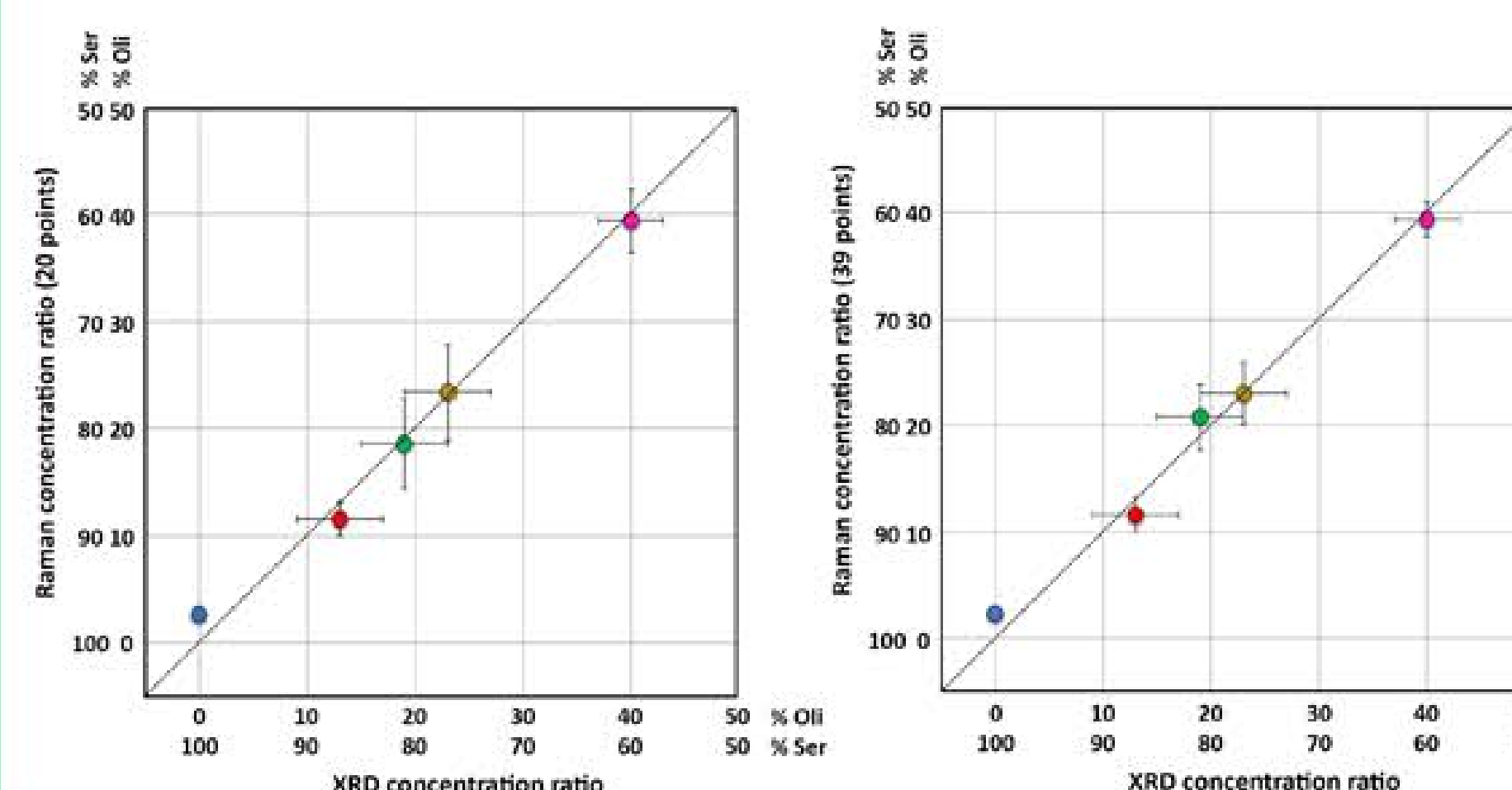
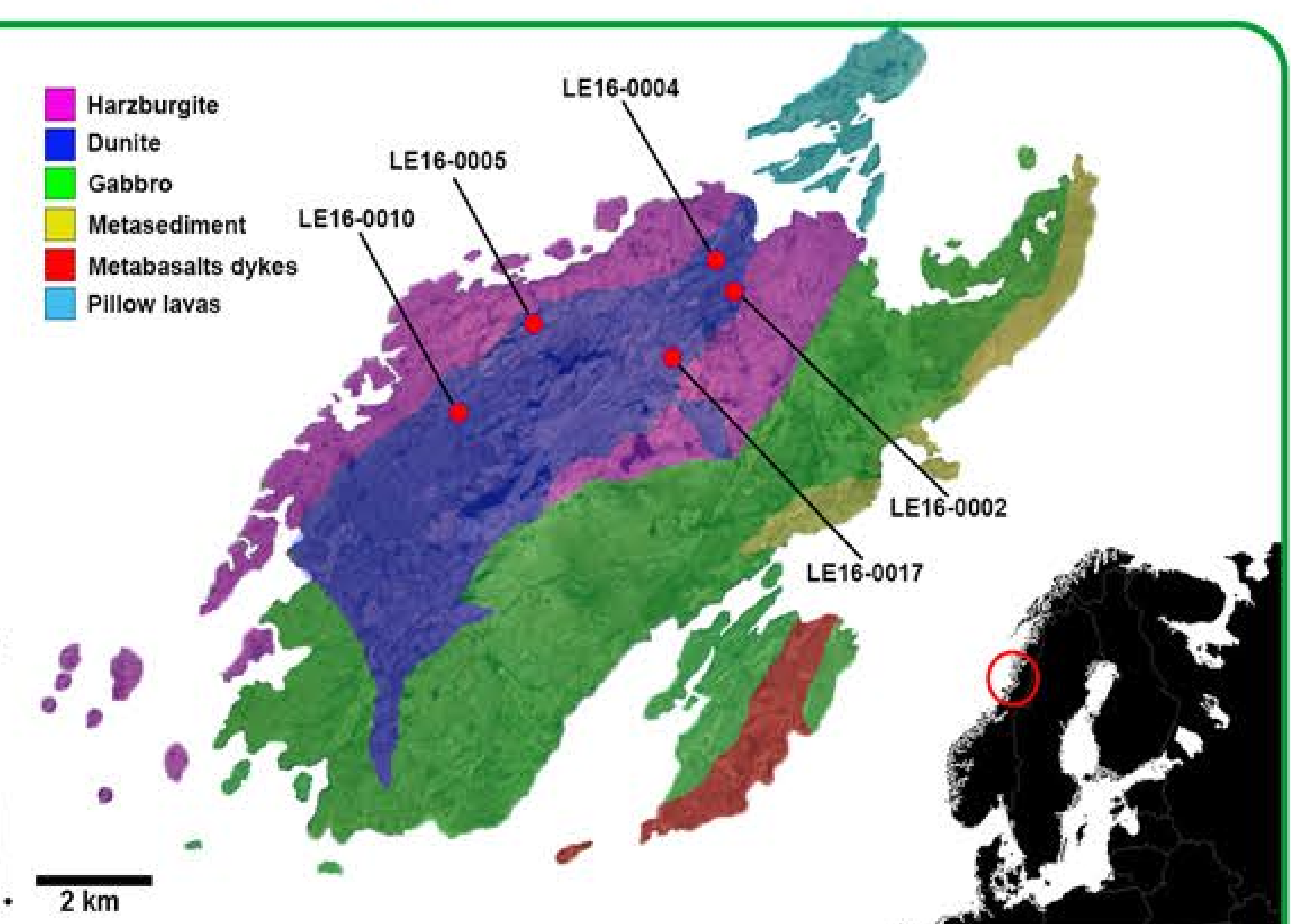
Profiting from the multi-point analysis performed by RLS on the sample, it is possible to establish analytical procedures to perform a semi quantification of the mineral abundance on sample mixtures. Calibration curves for the quantification of olivine and serpentine were prepared. In order to obtain (some degree of) statistical and uncertainty data for the calibration curves, we obtained five 39-point lines for each mixture proportion. The calibration curves were calculated following the univariate method by Lopez-Reyes et al. (Lopez-Reyes et al., 2013), in which the ratio between the intensity of non-overlapping peaks of the endmembers with respect to their total intensity are averaged for all the spectra along a n-point line



The obtained correlation coefficients (R^2) equal to 0.9993 (20 points) and 0.9995 (39 points) with an estimated uncertainty between $\pm 3.0\%$ and $\pm 5.2\%$ with a confidence interval of 95%.

Raman semiquantification of analogue picritic basalts from the Leka Ophiolite complex

Comparing RLS qualitative results with XRD data, we proved that the RLS ExoMars Simulator successfully identified all major phases (olivine and serpentine). Moreover, when emulating the automatic operating mode of the flight instrument, several additional compounds (pyroxene and brucite), were also detected.



Raman Calibration curves were used to determine the olivine/serpentine concentration ratio. As shown on the left, Raman results fit perfectly with XRD semiquantitative data.

Acknowledgments

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