



Yasumoto Tsukada,^a Stephen. A. Bowden^a and Patrick Schmidt^b

^a Geosciences, University of Aberdeen, Aberdeen, AB24 3UE, Scotland, ^bDepartment of Geosciences, Eberhard Karls University of Tübingen, Tübingen, Germany

Abstract

Microcrystalline and amorphous silica minerals include quartz, moganite and opal. Of these moganite is the most newly discovered mineral, with potential as an mineralogical indicator of diagenesis^[1], evaporitic depositional environments^[2] and even as an indicator for water on planetary bodies like the moon^[3]. Moganite can be measured by Raman spectroscopy as it has a Raman band at 501 cm⁻¹, but a band at 503 cm⁻¹ caused by silanol (SiOH) on the surface of minerals can mingle with the moganite complicating measurement^[4](Fig1,2). Here, we present a spectroscopic analysis of moganite and silanol bands co-occurring with quartz and explore methodologies to measure the three different crystal structures. Our results show a high sensitivity of Raman spectroscopy to silanol, but also that silanol is vulnerable to laser light. These physical and chemical differences allow the silica minerals to be differentiated.

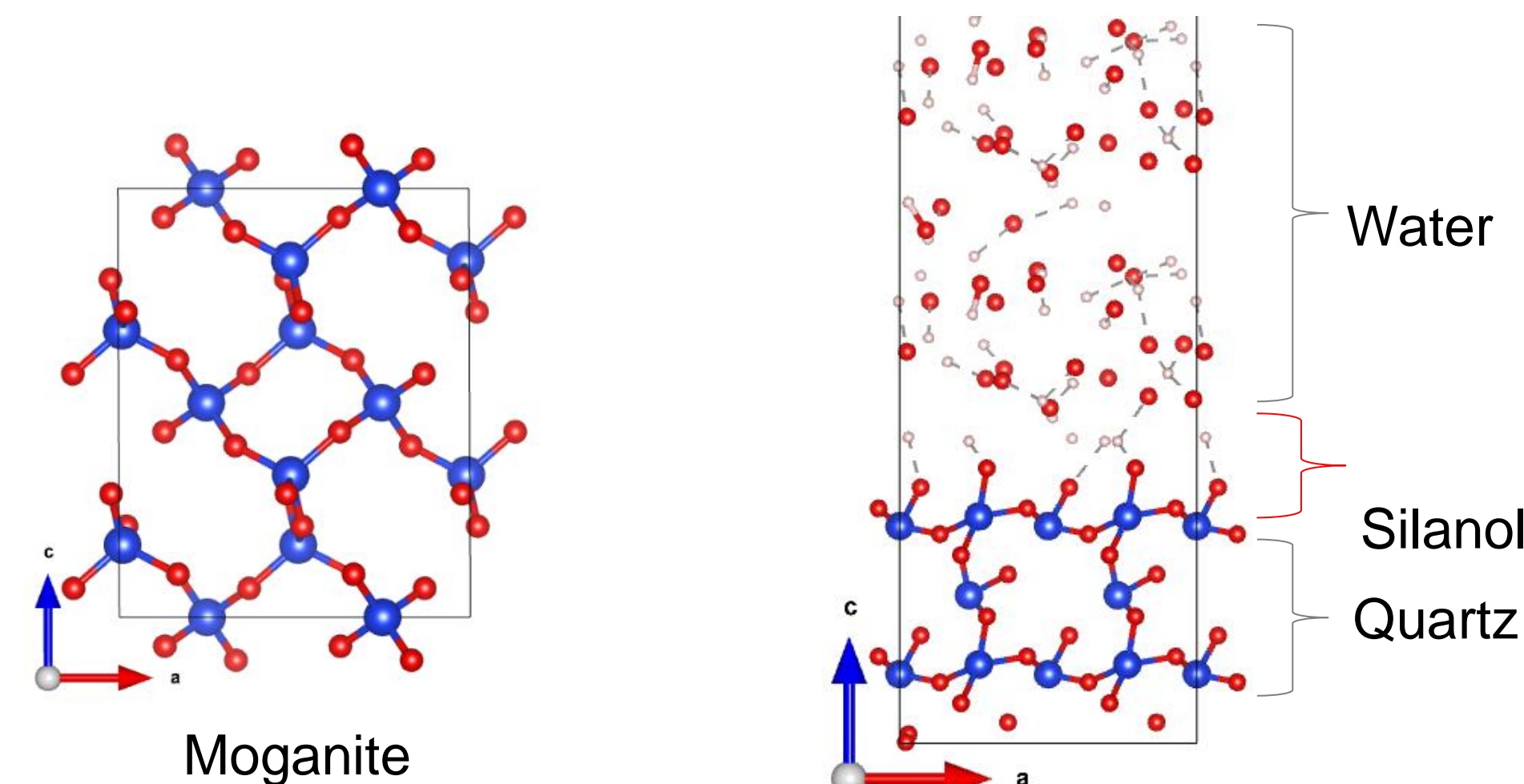


Fig1. Structure of moganite and silanol drawn by VESTA. The blue, red, and white balls represent Silica, Oxygen, and Hydrogen atoms.

Samples

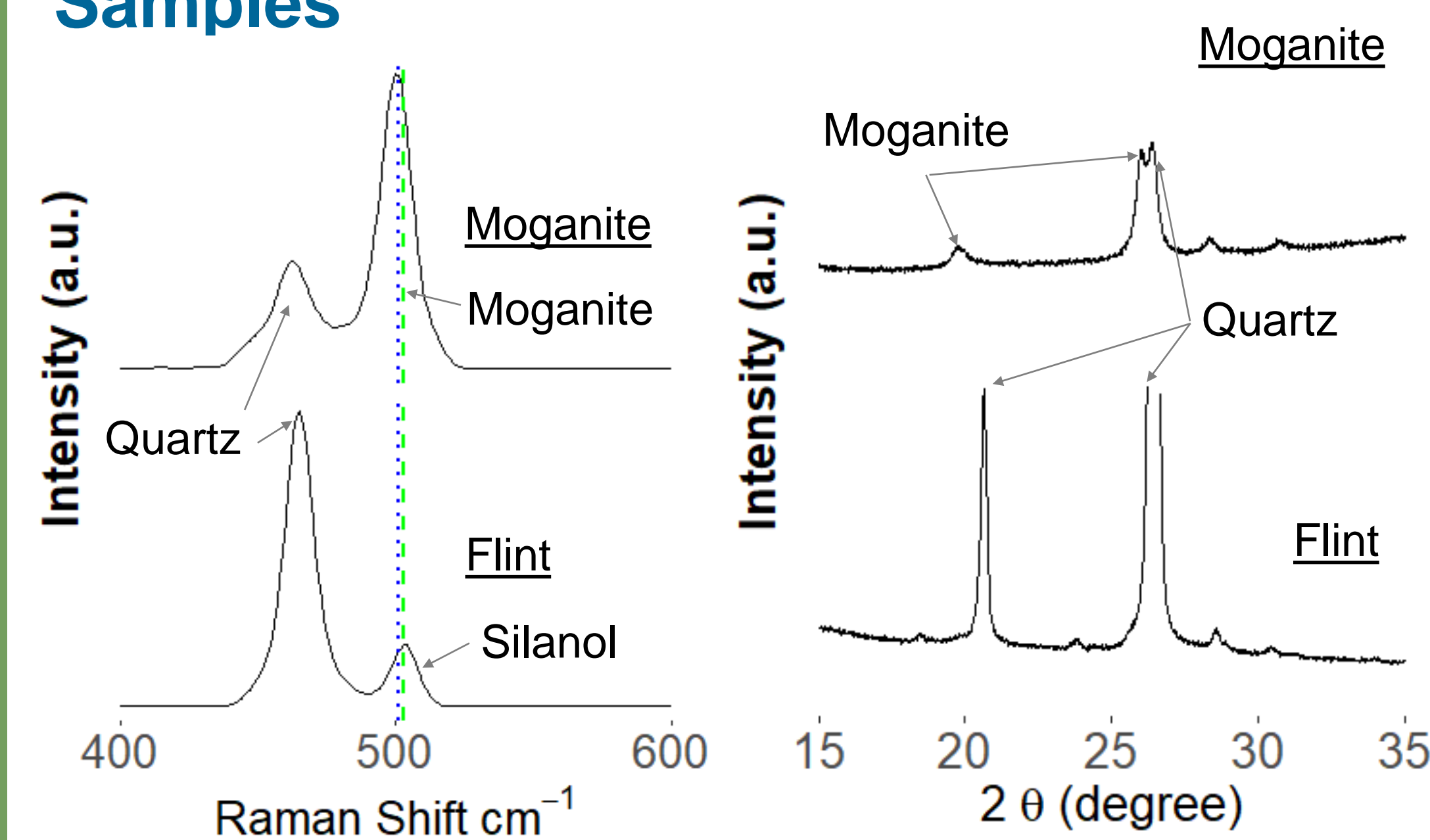


Fig2. Raman spectra (left) and X-ray diffraction pattern (right) of Moganite and Flint. Overlying blue dotted and green dashed lines are 501 & 503 cm⁻¹ respectively. Raman band identities at 501 cm⁻¹ for moganite and 503 cm⁻¹ for silanol in flint were also confirmed by powder X-ray diffraction.

Aim

1. Confirm diagnostic features of Raman spectra in moganite by observation and Ab-initio Molecular Dynamics (MD)
2. Identify differences between silanol and moganite, by exposing silanol surfaces by crushing

Methodology

1. Measure Raman Spectra on "pure" moganite^[5] and quartz, and perform Ab-initio Molecular Dynamics to obtain theoretically pure spectra
2. Raman Spectra measured on variably ground samples with different grain sizes and therefore surface areas with silanol groups (Fig3)

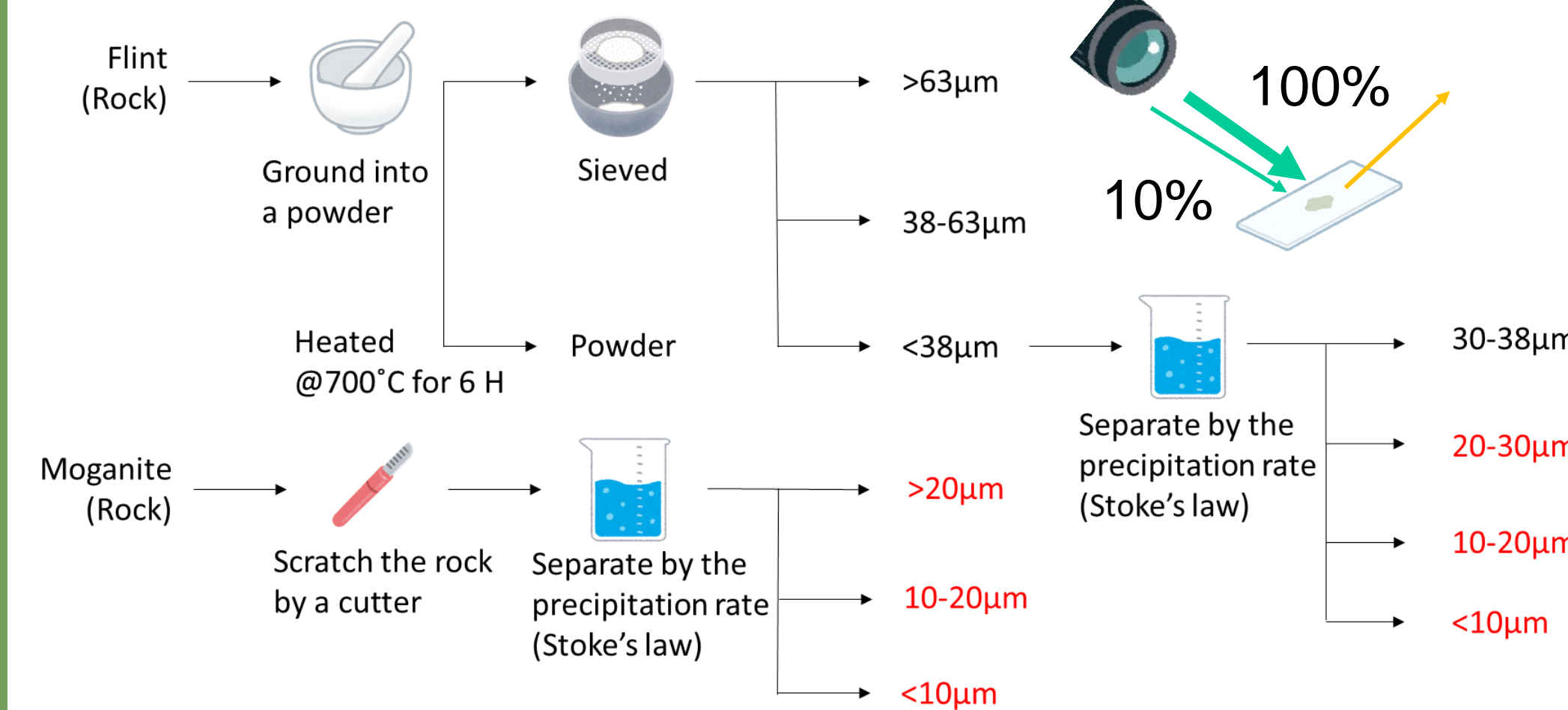


Fig3. Sample preparation of moganite and flint. The ground sample was acquired spectrum under the laser power of 10 & 100%.

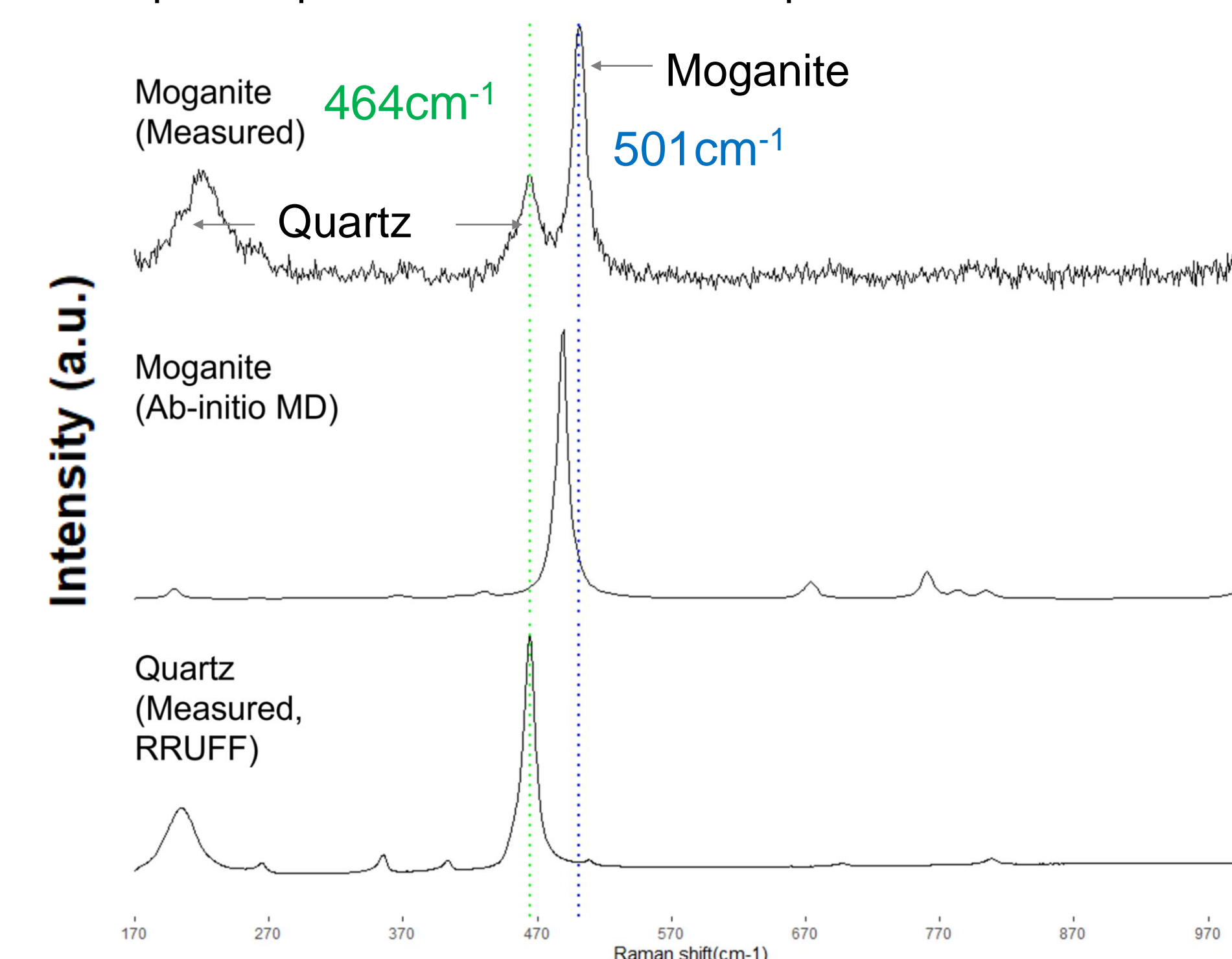


Fig4. Raman spectra of measured and simulated moganite and reference quartz (https://rruff.info).

Pure moganite is not common and natural samples of moganite cooccur with quartz^[6](Fig4). Ab-initio Molecular Dynamic modelling yields a Raman spectra suggesting that moganite itself has little effect on quartz spectra, except for peak at 501 cm⁻¹.

Results

Peak heights, widths and centres were calculated for Raman spectra measured on different particle sizes. Lorentzian curves were fitted to spectra after baseline subtraction and height normalization.

As the particle size decreased the size of silanol peaks increased, relative to small fluctuations observed in moganite (Fig5). This is consistent with newly formed silanol sites generated by exposing fresh quartz-surfaces as surface area increases.

Decreases in Raman-shift (peak position) and increases in FWHM in moganite spectra can be attributed to a phase change from α to β moganite^[7], while broadening in silanol peaks below particle sizes < 10 μ m shows the loss of the silanol bands^[4](Fig6). Previous work has shown similar effects to be triggered in quartz by laser-induced heating^[8]. Notably moganite and silanol data do not overlap.

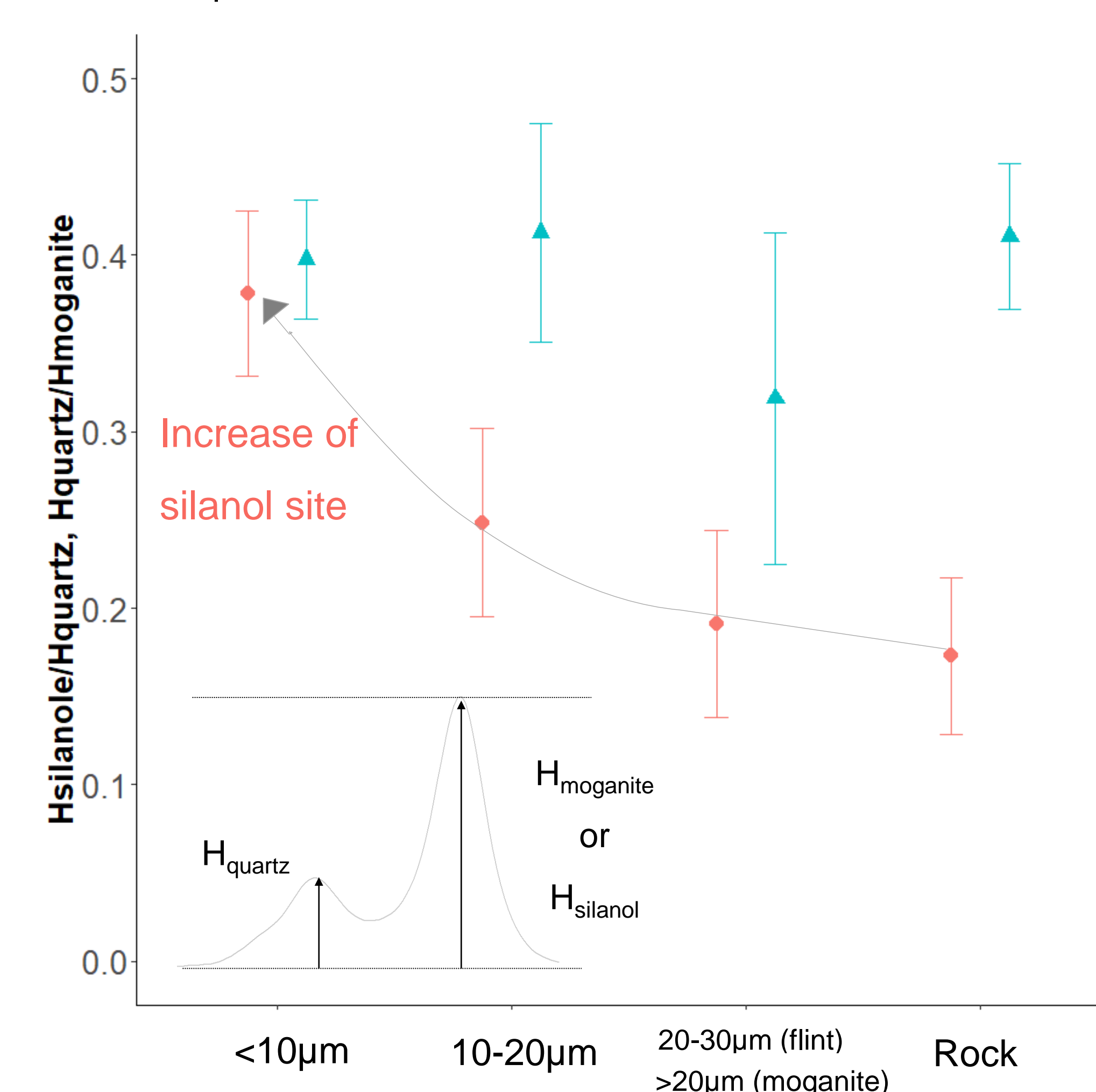


Fig5. Comparison of peak height by different particle size at 10% laser power.

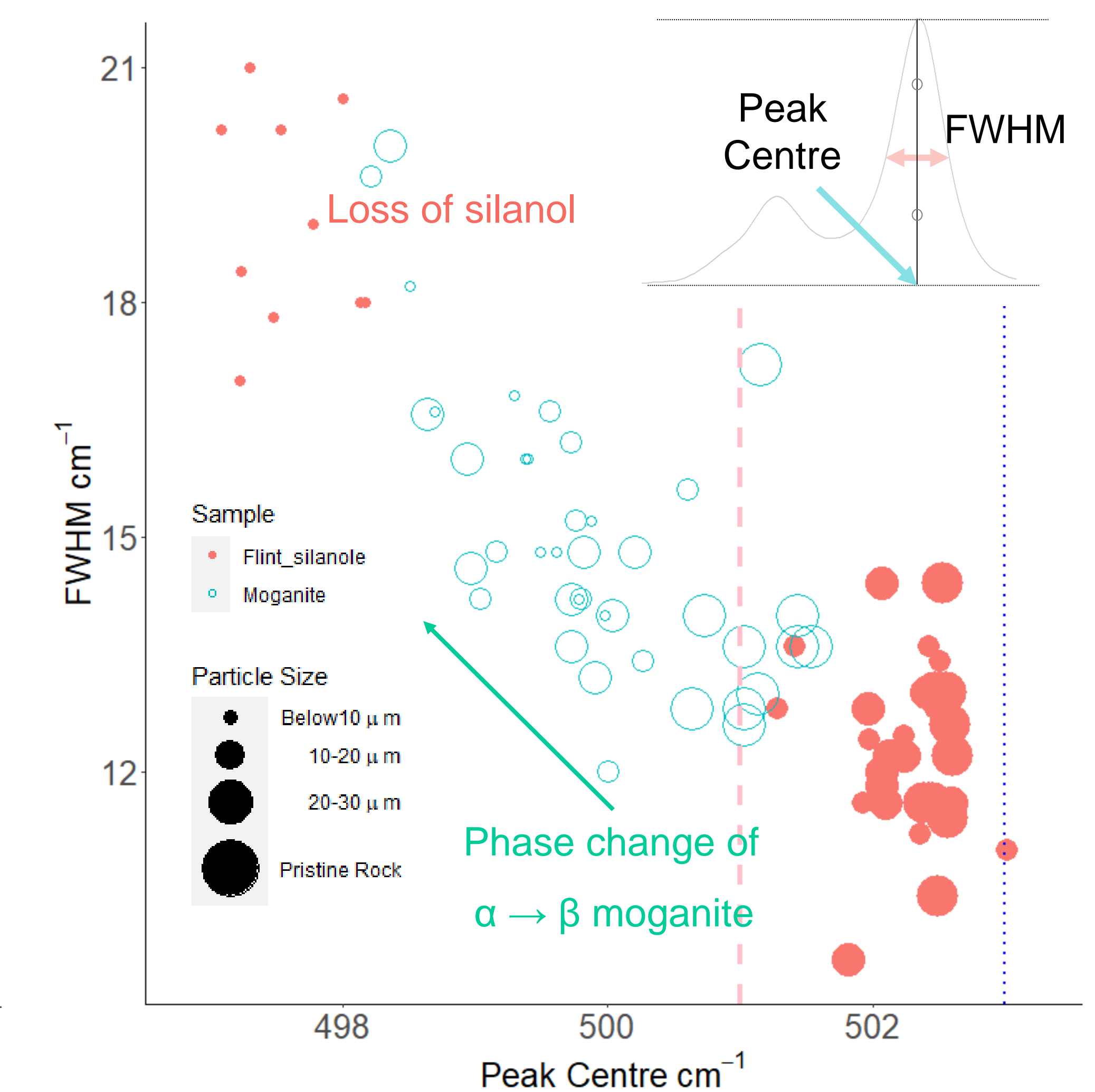


Fig6. Peak width and centre of moganite and silanol at 100% laser power.

Conclusions

- Particle size effects and laser-induced heating differentiate moganite silanol bearing samples. Crushing and sorting particles to <10 μ m can therefore differentiate moganite and silanol, but this requires powder or scratched samples.
- Raman spectroscopy can potentially quantify silanol sites and provide information on the surface properties of quartz by measuring bands at 503 (silanol) /464 (quartz) cm⁻¹.

Reference

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