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Supplementary Materials for

Biosignature stability in space enables their use for life detection on Mars

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Supplementary Text

Rationale for the selection of the biogenic compounds

The selection of the tested compounds focused on their definite biological origin. While numerous nucleic acid compounds (pyrimidines and purines), α- and other amino acids, carboxylic acids, aldehydes, alcohols, and simple sugars as well as (often polycyclic aromatic) hydrocarbons were reported to be formed abiotically in interstellar, circumstellar and protoplanetary clouds(*52*), in meteorites(*53*), as well as on early Earth(*54*) and Mars(*55*), none of the presently selected substances have been reported to date in space or on planetary bodies, thus predestining them as potential biomarkers. Moreover, amino acids and nucleobases have already been characterized by Raman spectroscopic techniques(*56*) and extensively considered in the contexts of astrochemistry/-biology(*57*) and Mars(*58*). Therefore, neither of these substance classes was included in the present study.

Photoprotective pigments, such as carotenoids, have been extensively used as model biosignatures due to their known stability and excellent identification by Raman spectroscopy (especially with a 532 nm laser excitation due to resonance effects): from *in situ* measurements in martian analogue environments to laboratory investigations, even when embedded in the mineral matrix(*59*). Carotenoids and fossil carotenoids (such as carotane) have high preservation potential as shown from terrestrial examples where they were successfully identified with gas chromatography / mass spectrometry (GC/MS) and Raman spectroscopy in 1.44 million-year-old halite brine inclusions(*60*) and in 1.64-billion-year-old samples, respectively(*61*). Carotenoids can thus serve as a signature for both extant life and extinct life, in their diagenetically altered form coined biomarkers(*59*, *62*). In addition, they represent a very large class of pigments, with more than 750 different chemical structures determined to date. Due to their distribution in very diverse organisms, including extremophiles, and the several key functions they serve at the cellular level, it has been proposed that carotenoids played an important role in the early evolution of life on Earth(*63*). Indeed, they have excellent antioxidant properties (*64*), which may have been essential for the highly UV irradiated early Earth organisms(*65*), and may have played an early role in membrane stabilization, prior to fatty acids(*66*).

Similarly, the polymer melanin, present in all domains of terrestrial life, is a common light- and UV-protective constituent of astrobiological models such as *Cryomyces antarcticus*(*67*), *Cryptomyces minterii*, *Rhizocarpon geographicum* and *Buellia frigida*(*68*). These organisms have shown extensive resistance to simulated and real space stressors, in particular ionizing radiation, thanks, in part, to their melanin pigmentation. Interestingly, the insoluble organic matter fraction found in carbonaceous chondrites presents similarities to the primary precursors of bacterial and fungal melanins (allomelanins) and may point towards a very early origin of melanin pigments used by terrestrial, and potentially martian, life(*69*).

The blue-light and UV-protective secondary lichen compound parietin, found in the astrobiologically relevant lichens *Xanthoria elegans*(*70*) and *Fulgensia bracteata*(*43*), and the free radical scavenging flavonoids quercetin and naringenin, are all widely distributed in terrestrial life and play essential roles in UV and ionizing radiation resistance.

Chlorophylls are ubiquitous in light harvesting reactions in terrestrial life. At their central structure is an aromatic ring system with a sequestered metal atom, called a porphyrin. Porphyrins were originally regarded as ideal biomarkers(*71*) due to their high preservation potential in the geological record, as geoporphyrins(*45*), and the fact that no abiotic formation route had been discovered. New laboratory experiments have however disputed these conclusions and shown their potential abiotic formation under specific conditions, suggesting caution when interpreting potential porphyrin signals(*72*). These results also suggest that precursors of chlorophylls and hemes could have been available to the first protocells, which is consistent with the proposed first functions of porphyrins and related pigments in early terrestrial life as UV-protective rather than light-harvesting molecules(*73*).

The two other selected biogenic compounds are structural polysaccharides. Cellulose, as the most common biopolymer on Earth(*74*), is an extracellular polymeric substance produced by phylogenetically diverse bacteria of the genera *Gluconacetobacter*, *Agrobacterium*, *Pseudomonas*, *Rhizobium, Azotobacter*, *Salmonella*, *Alcaligenes* and *Sarcina*, the sulphur-oxidizing bacteria(*75*), and cyanobacteria(*76*). Cellulose-producing microorganisms inhabit seawater, hot springs, drylands and other extreme econiches. Microbial cellulose has remarkable physical properties, explaining its stability under high temperatures and pressures, irradiation, and other stressors providing extensive protection to cellulose-synthesizer organisms(*77*). Cellulose might thus have played an important role in the survival of microbial organisms in the harsh conditions of primordial Earth around 3.5 billion years ago and is presumably one of the oldest native macromolecule found on Earth(*78*). Chitin, one of the main constituents of the cell walls of the astrobiological model fungi and lichens mentioned above, has also been reported in organically preserved fossils(*79*) and might play an important role in biomineralization processes, relevant for biosignatures preservation(*80*).

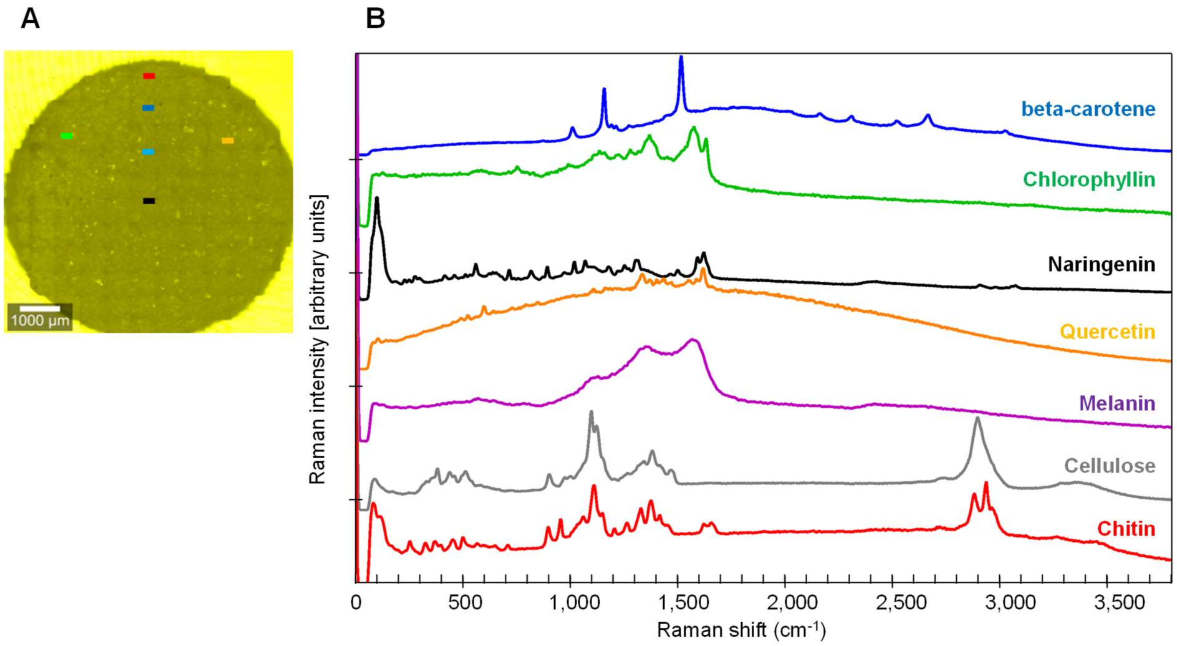


Fig. S1. Raman spectra of pure investigated biogenic compounds: (A), Example of six 200µm-Line scans on a pellet sample. **(B)**, Stacked spectra with different scales acquired with a confocal WITec alpha 300 system at 532 nm excitation wavelength and measurement as reported in Material and Methods.

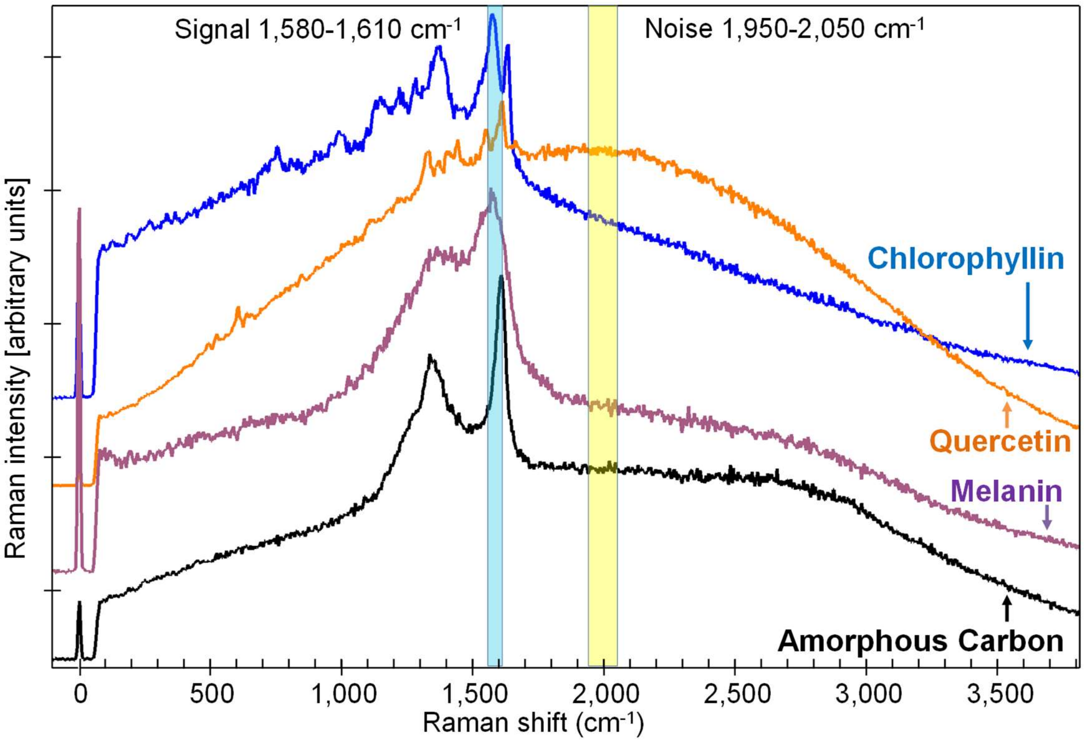


Fig. S2. Filter regions used in the WITec Project FIVE software to identify the biomolecules signal of interest: main region used for signal recognition in blue and region used for noise calculation in yellow. Examples of unprocessed spectra of (from top to bottom): chlorophyllin (in blue), quercetin (in orange), melanin (in purple), and amorphous Carbon (in black).

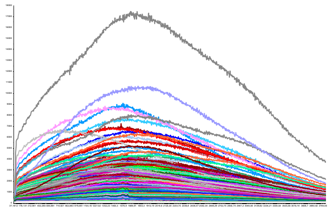
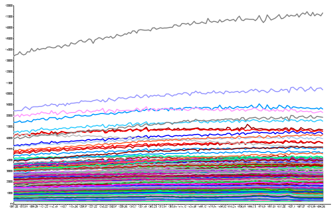
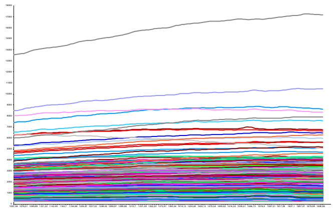
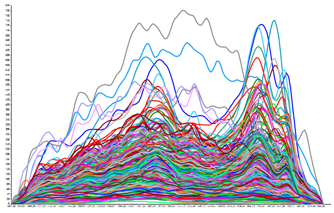
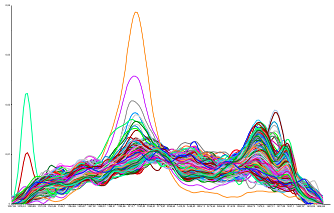
1		Raw data 0-3,800cm^{-1}
2		Raw data specifics 1,050-1,700cm^{-1}
3		Raw data specifics 1,050-1,700cm^{-1} Smoothed Gaussian Filter segment size 9
4		Raw data specifics 1,050-1,700cm^{-1} Smoothed Gaussian Filter segment size 9 Baseline Offset & Linear Baseline Correction
5		Raw data specifics 1,050-1,700cm^{-1} Smoothed Gaussian Filter segment size 9 Baseline Offset & Linear Baseline Correction Area Normalization

Fig. S3. Preprocessing steps illustration on Unscrambler, example on a test set (600 out of 6,000 spectra) for chlorophyllin samples.

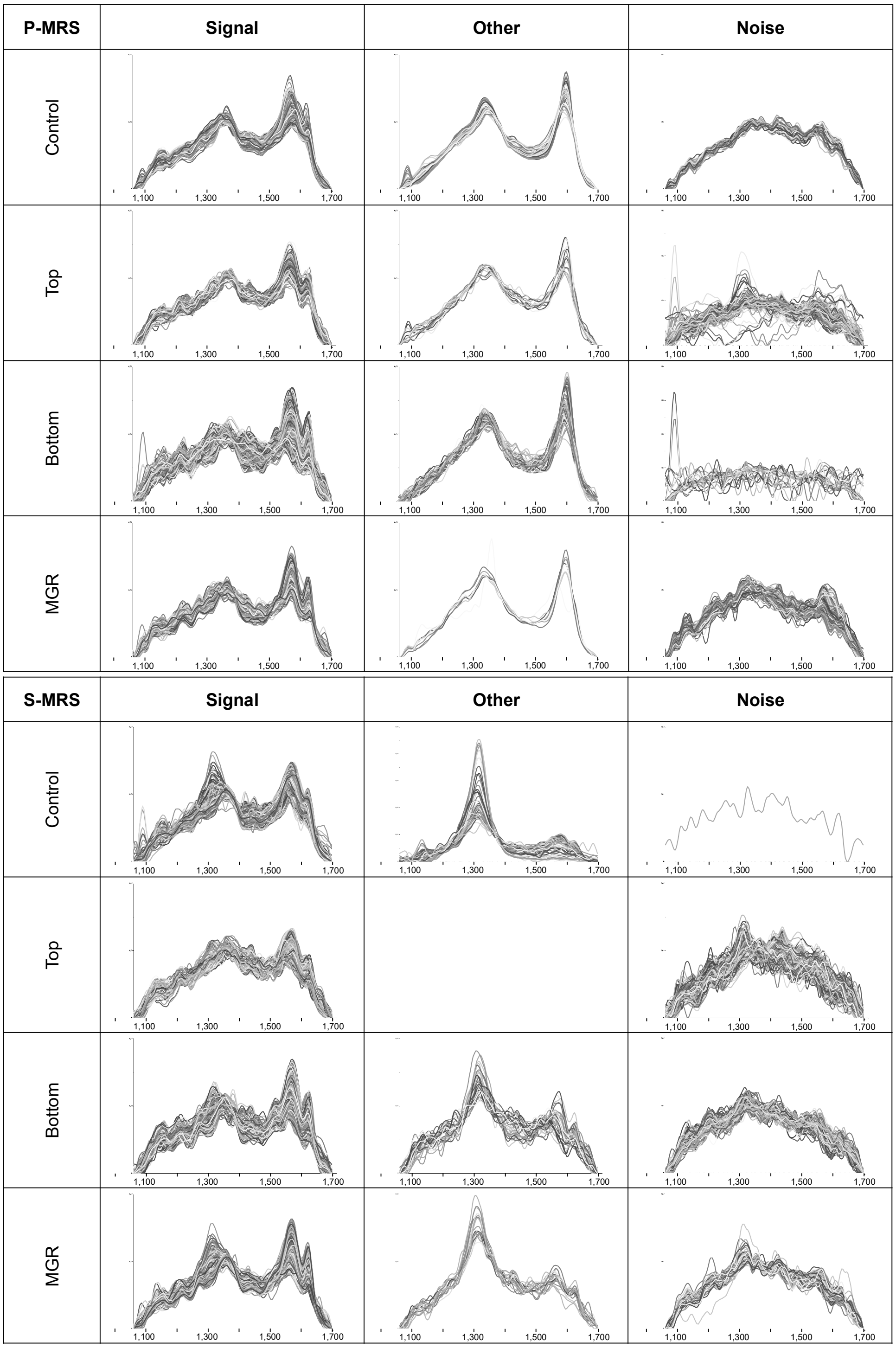


Fig. S4. Identified classes for chlorophyllin on P-MRS and S-MRS. Rows show the different sample types (Control, Top, Bottom, and MGR) while columns show the identified classes (Signal, Other, and Noise). Preprocessed spectra with the region of interest 1,050-1,700 cm^{-1}.

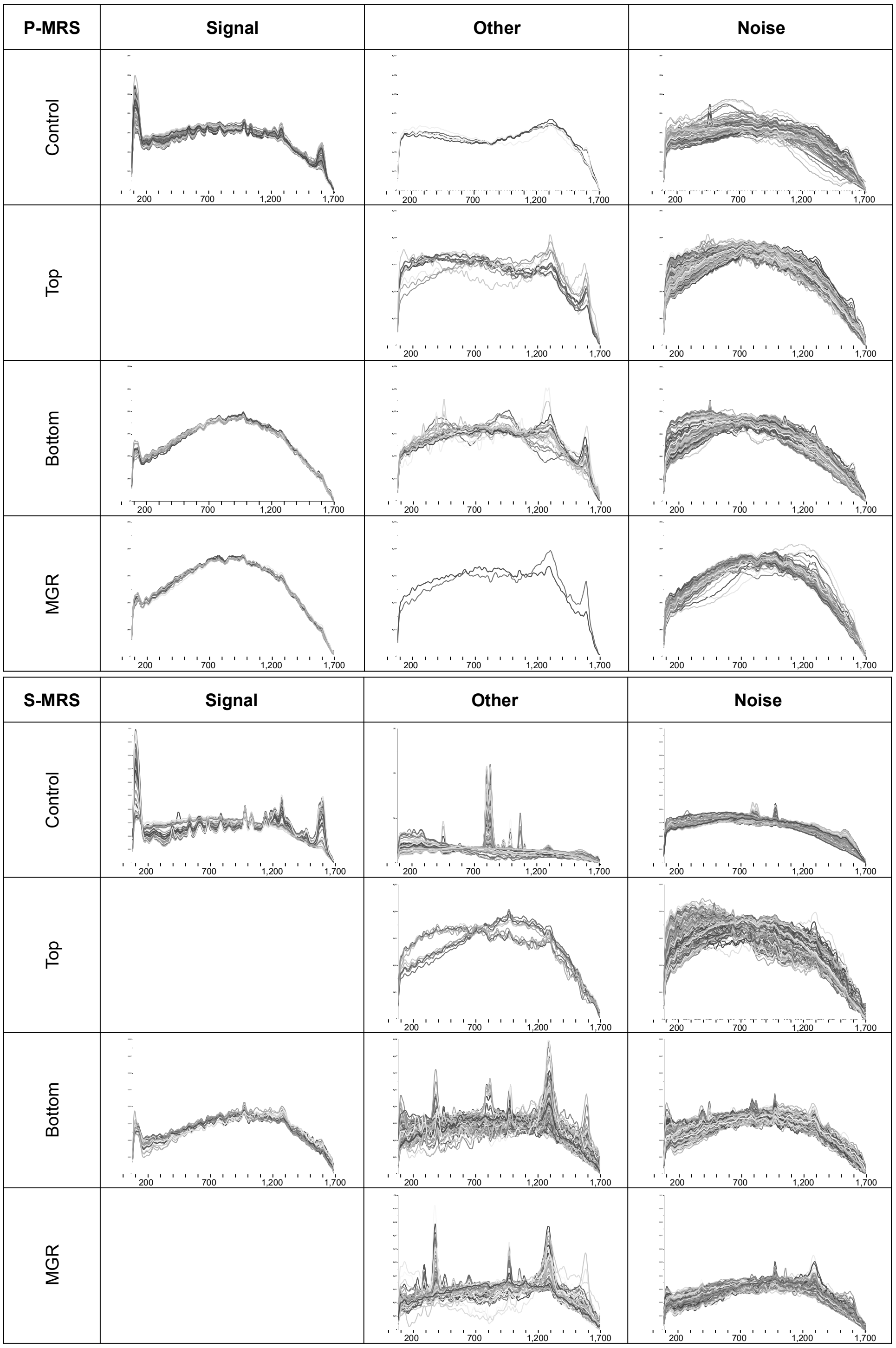


Fig. S5. Identified classes for naringenin on P-MRS and S-MRS. Rows show the different sample types (Control, Top, Bottom, and MGR) while columns show the identified classes (Signal, Other, and Noise). Preprocessed spectra with the region of interest 60-1,700 cm^{-1}.

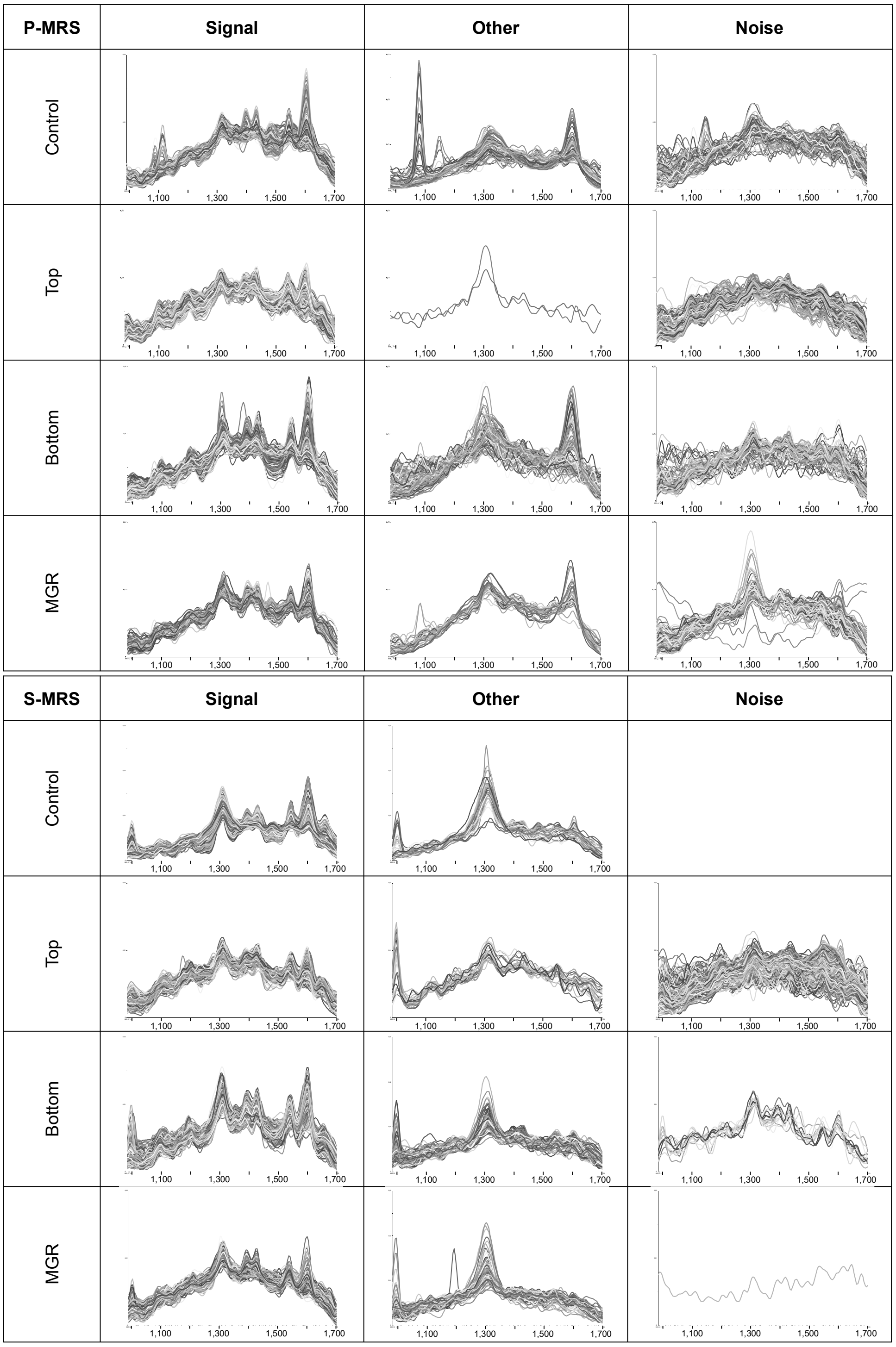


Fig. S6. Identified classes for quercetin on P-MRS and S-MRS. Rows show the different sample types (Control, Top, Bottom, and MGR) while columns show the identified classes (Signal, Other, and Noise). Preprocessed spectra with the region of interest 1,000-1,700 cm^{-1}.

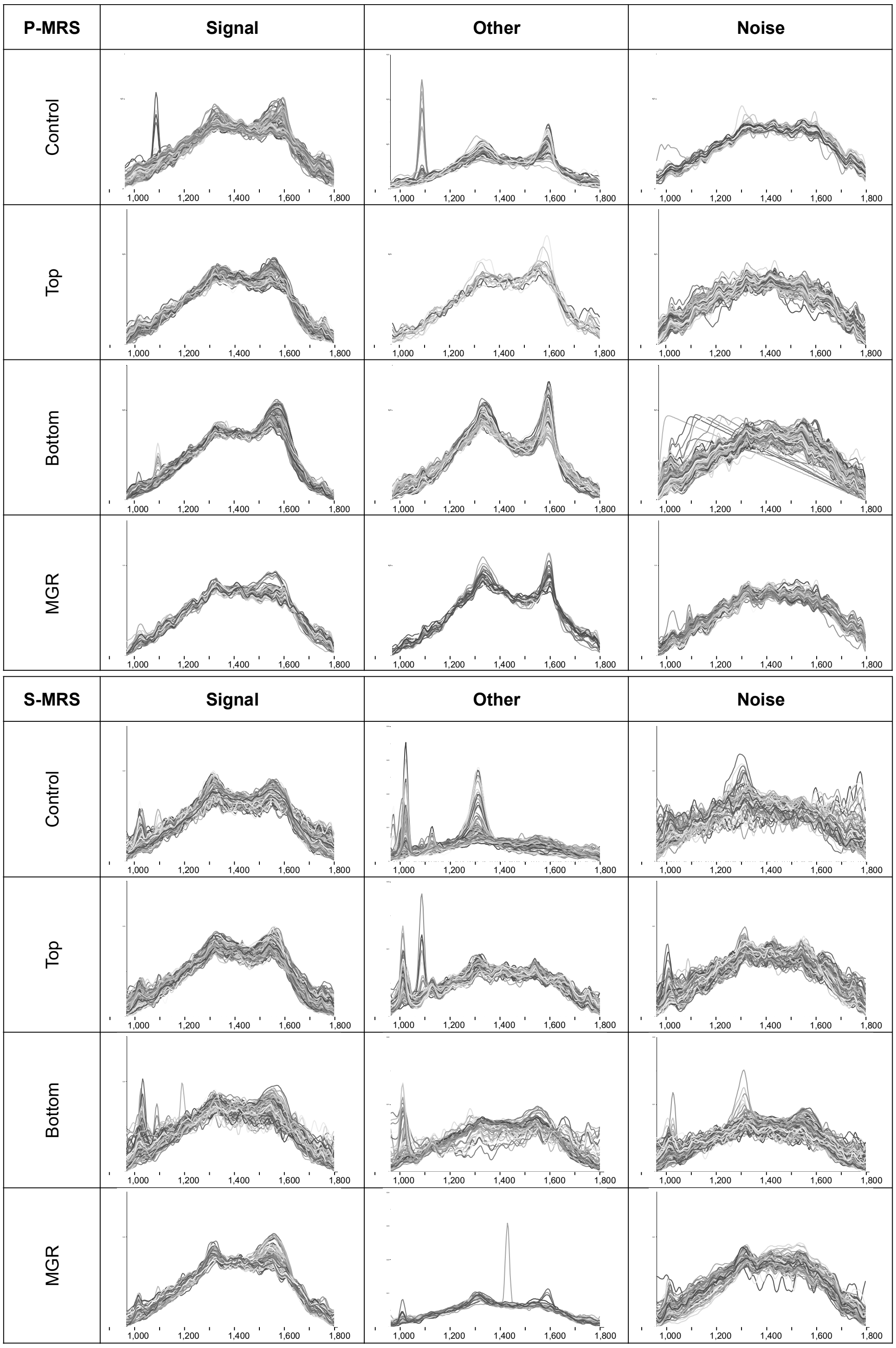


Fig. S7. Identified classes for melanin on P-MRS and S-MRS. Rows show the different sample types (Control, Top, Bottom, and MGR) while columns show the identified classes (Signal, Other, and Noise). Preprocessed spectra with the region of interest 950-1,800 cm^{-1}.

Table S1. Mars regolith simulants (MRS)

Component	Phyllosilicatic MRS (wt/v %) Early Mars	Sulfatic MRS (wt/v %) Late Mars
Pyroxene, Plagioclase, Amphibole, Ilmenite (Gabbro)	3	32
Olivine $(Mg,Fe)_2SiO_4$	2	15
Quartz SiO_2	10	3
Hematite Fe_2O_3	5	13
Montmorrilonite $[(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \text{ x } H_2O]$	45	-
Chamosite $[(Fe^{2+},Mg,Fe^{3+})5Al(Si_3Al)O_{10}(OH,O)_8]$	20	-
Kaolinite $Al_2Si_2O_5(OH)_4$	5	-
Siderite $Fe(CO_3)$	5	-
Hydromagnesite $Mg_5(CO_3)_4(OH)_2 \text{ x } 4H_2O$	5	-
Goethite FeO(OH)	-	7
Gypsum $Ca(SO_4) \text{ x } 2H_2O$	-	30

Table S2. Differences in signal coverage between clustering and filtering methods: differences between combined datasets for clustering and filtering methods.

		Clustering	Filtering	Absolute difference
Chlorophyllin	PMRS Control	83.4%	76.2%	7.2%
	PMRS Top	26.9%	37.7%	10.8%
	PMRS Bottom	90.2%	74.3%	16.0%
	PMRS MGR	68.4%	63.2%	5.2%
	SMRS Control	89.6%	81.7%	7.9%
	SMRS Top	48.9%	44.1%	4.8%
	SMRS Bottom	76.9%	75.6%	1.3%
	SMRS MGR	72.2%	71.5%	0.7%
Naringenin	PMRS Control	24.6%	21.7%	2.9%
	PMRS Top	0.0%	0.0%	0.0%
	PMRS Bottom	2.4%	0.0%	2.4%
	PMRS MGR	2.4%	0.2%	2.2%
	SMRS Control	12.6%	12.0%	0.6%
	SMRS Top	0.0%	0.0%	0.0%
	SMRS Bottom	3.9%	3.5%	0.4%
	SMRS MGR	0.0%	7.2%	7.2%
Quercetin	PMRS Control	59.4%	48.2%	11.2%
	PMRS Top	29.2%	20.3%	9.0%
	PMRS Bottom	70.0%	70.1%	0.1%
	PMRS MGR	34.0%	25.0%	9.0%
	SMRS Control	90.8%	94.0%	3.2%
	SMRS Top	28.8%	22.0%	6.8%
	SMRS Bottom	81.9%	69.3%	12.6%
	SMRS MGR	73.4%	71.5%	1.9%
Melanin	PMRS Control	60.2%	57.5%	2.7%
	PMRS Top	9.5%	5.3%	4.2%
	PMRS Bottom	10.5%	11.1%	0.6%
	PMRS MGR	14.4%	10.6%	3.8%
	SMRS Control	55.0%	47.7%	7.3%
	SMRS Top	38.8%	35.5%	3.3%
	SMRS Bottom	22.8%	23.2%	0.4%
	SMRS MGR	34.2%	19.5%	14.7%
			Average:	**5.0%**

Table S3. Differences in signal coverage between anoxic and oxic sets according to the method (clustering or filtering).

Chlorophyllin			**Clustering**	
		Anoxic	Oxic	Difference
	PMRS Top	30.2%	23.6%	6.6%
	PMRS Bottom	90.6%	89.8%	0.8%
	SMRS Top	56.8%	41.0%	15.8%
	SMRS Bottom	81.8%	72.0%	9.8%
			Filtering	
		Anoxic	Oxic	Difference
	PMRS Top	39.0%	36.7%	2.3%
	PMRS Bottom	75.5%	73.0%	2.5%
	SMRS Top	51.8%	39.0%	12.8%
	SMRS Bottom	78.2%	73.0%	5.2%
Naringenin			**Clustering**	
		Anoxic	Oxic	Difference
	PMRS Top	0.0%	0.0%	0.0%
	PMRS Bottom	0.0%	4.8%	-4.8%
	SMRS Top	0.0%	0.0%	0.0%
	SMRS Bottom	0.2%	7.6%	-7.4%
			Filtering	
		Anoxic	Oxic	Difference
	PMRS Top	0.0%	0.0%	0.0%
	PMRS Bottom	0.0%	0.0%	0.0%
	SMRS Top	0.0%	0.0%	0.0%
	SMRS Bottom	0.0%	10.5%	-10.5%
Quercetin			**Clustering**	
		Anoxic	Oxic	Difference
	PMRS Top	35.6%	22.8%	12.8%
	PMRS Bottom	61.0%	79.0%	-18.0%
	SMRS Top	17.0%	40.6%	-23.6%
	SMRS Bottom	77.8%	86.0%	-8.2%
			Filtering	
		Anoxic	Oxic	Difference
	PMRS Top	17.8%	22.7%	-4.8%
	PMRS Bottom	66.2%	74.0%	-7.8%
	SMRS Top	23.3%	20.7%	2.7%
	SMRS Bottom	74.0%	93.0%	-19.0%
Melanin			**Clustering**	
		Anoxic	Oxic	Difference
	PMRS Top	12.2%	6.8%	5.4%
	PMRS Bottom	16.2%	4.8%	11.4%
	SMRS Top	60.4%	17.2%	43.2%
	SMRS Bottom	34.4%	11.2%	23.2%
			Filtering	
		Anoxic	Oxic	Difference
	PMRS Top	7.5%	3.6%	3.9%
	PMRS Bottom	10.1%	12.1%	-2.0%
	SMRS Top	46.5%	20.8%	25.7%
	SMRS Bottom	29.4%	14.3%	15.1%

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