Chemical Data Collections Manuscript

Title: *Raman Microspectroscopic Mapping with Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) of the High-Pressure, α -PbO₂-Structured Polymorph of Titanium Dioxide, TiO₂-II*

Authors: Joseph P. Smith¹, Frank C. Smith², Alexandra E. Krull-Davatzes³, Bruce M. Simonson⁴, Billy P. Glass² and Karl S. Booksh^{1*}

Affiliations: ¹Department of Chemistry & Biochemistry, University of Delaware, 002 Lammot du Pont Laboratory, Newark DE 19716, USA

²Department of Geological Sciences, University of Delaware, 255 Academy Street, Newark DE 19716, USA

³Department of Earth and Environmental Science, Temple University, 1901 N. 13th Street, Philadelphia, Pennsylvania 19122, USA

⁴Geology Department, Oberlin College, 52 W. Lorain Street, Oberlin, Ohio 44074, USA

***Corresponding author. Tel: (302) 831-2561 Email: kbooksh@udel.edu**

Abstract

The recent identification of the high-pressure, α -PbO₂-structured polymorph of titanium dioxide, TiO₂-II, in grains recovered from four Neoarchean spherule layers has provided physical evidence to further support an impact origin of these layers. Smith et al. (2016, in press) investigated these TiO₂-II-bearing grains using Raman microspectroscopic mapping with multivariate curve resolution-alternating least squares (MCR-ALS) to spatially and spectrally resolve the individual chemical species within the grains. Here we provide the Raman microspectroscopic mapping data collected on the TiO₂-II-bearing grains. We further provide chemical maps, chemical images and Raman spectra of rutile, TiO₂-II, anatase, quartz, and substrate-adhesive epoxy that were resolved using MCR-ALS applied to the Raman microspectroscopic mapping data. The Raman microspectroscopic mapping data in this work—collected using both high spectral resolution and high spatial resolution—provides a myriad of opportunities for the scientific community in wide ranging applications, including the chemical imaging and chemometric disciplines.

Graphical abstract

Keywords

Chemical imaging; Raman microspectroscopy; Multivariate curve resolution-alternating least squares (MCR-ALS); Titanium dioxide (TiO_2); High-pressure polymorph

Specifications Table

Subject area	<i>Analytical Chemistry, Spectroscopy, Chemometrics</i>
Compounds	<i>Titanium dioxide polymorphs (rutile, anatase, TiO_2-II), silicon dioxide polymorph (quartz), and substrate-adhesive epoxy</i>
Data category	<i>Raman microspectroscopic mapping data, Spectral data</i>
Data acquisition format	<i>Raman spectra</i>
Data type	<i>Raw</i>
Procedure	<i>Hyperspectral imaging; acquire Raman spectra over a desired area of samples to ultimately form chemical maps of the respective species within the probed area</i>
Data accessibility	<i>Data is directly available within article</i>

Rationale

Titanium dioxide (TiO_2) is extensively utilized in a variety of applications, ranging from photocatalysis to water splitting reactions.[1-3] Rutile, anatase, and brookite are the main natural TiO_2 polymorphs, with rutile being most abundant.[4] Five high-pressure polymorphs of TiO_2 exist.[5, 6] A primary focus of this work is the orthorhombic, $\alpha\text{-PbO}_2$ -structured high pressure polymorph, termed TiO_2 -II, which has recently gained momentum due to its stability at ambient pressure and temperature.[7]

Natural TiO₂-II has been documented in both ultrahigh-pressure metamorphic[8-11] and shock-metamorphosed[12-15] materials. Recently, shock-metamorphosed grains containing rutile and TiO₂-II have been documented from four Neoarchean spherule layers—Carawine spherule layer (CSL), Jeerinah spherule layer (JSL), Monteville spherule layer (MSL), and Bee Gorge spherule layer (BGSL)—deposited between ~2.65 and ~2.54 billion years ago.[16] These grains, which provide unambiguous physical evidence to further support an impact origin for these layers[16], comprise the samples for this study.

Raman microspectroscopic mapping is employed in various research areas, including biological and materials sciences.[17-21] Multivariate analysis methods, including MCR-ALS, applied to Raman microspectroscopic mapping can provide spatially resolved chemical images and spectra of the individual chemical species within a sample.[21-25] Recently, Smith et al. were the first to employ Raman microspectroscopic mapping with MCR-ALS to determine the distribution of TiO₂-II in these shock-metamorphosed grains, in which spectral profiles and spatially-resolved chemical maps of rutile, TiO₂-II, anatase, quartz, and substrate-adhesive epoxy were generated at different spatial resolutions.[26]

In this work, we present the Raman microspectroscopic mapping data—in raw spectral data format—collected on the TiO₂-II-bearing grains and the results of MCR-ALS applied to this Raman microspectroscopic mapping data on a selected grain from the MSL. We offer a comparison between high spectral and high spatial resolution mapping data, and a discussion of the data's importance to the scientific community.

Procedure

Sample Preparation. Uncoated, polished grain mounts of selected TiO₂-II-bearing grains identified by Smith et al.[16] were made. In brief, grains were fixed to a glass slide (Fisher Scientific, 25.4 mm diameter x 1.0 mm thick) using epoxy (Buehler), and polished to expose the grains. Details of locations, lithologies, and preparation are given in Smith et al.[16] A summary of the sample preparation is given in the Supplemental Material.

Scanning electron microscopy (SEM). Backscattered electron (BSE) images, collected using an FEI Quanta 450 FEG scanning electron microscope operated at 10-30 kV and low vacuum, were obtained for TiO₂-II-bearing grains in the polished grain mounts.

Raman microspectroscopic mapping. A Senterra Raman spectrometer (Bruker Optics, Massachusetts, USA) coupled to a BX-51 microscope (Olympus, New York, USA) was used for all Raman microspectroscopic mapping measurements. A 532 nm laser excitation source was focused onto the sample using objective lenses (Olympus, New York, USA). The objective lenses, with numerical apertures (NA) listed, were 20× (0.40 NA), 50× (0.75 NA), and 100× (0.80 NA) magnification, which yield a laser spot size of 5 μm, 2 μm, and 1 μm in diameter, respectively. Scattered light from the sample was collected by the objective lens, dispersed by a 1200 grooves/mm grating, and detected by a charge-coupled device (CCD) detector (Bruker Optics, Massachusetts, USA) thermoelectrically-cooled to – 65 °C. A constant laser power of 2 to 10 mW was used. Integration times of 1 to 15 seconds with 0 to 3 co-averages were used. Background measurements equal to the respective integration time were acquired for each measurement. In total, the collection time for each Raman spectrum was ~6 to 90 seconds. A spectral region of 70-1550 cm⁻¹, covered under one grating position, was used for all measurements.

Excitation wavelength and wavenumber calibration were internally performed using a neon lamp prior to each measurement. Ultimately, the spectral resolution of each Raman spectrum was 3 to 5 cm⁻¹.

Raman microspectroscopic mapping data was generated using rectangular grids with assigned size and locations for the collection of Raman spectra based on the dimensions of the grain being analyzed. The step size between collected Raman spectra within a spectral grid was ~1 to 4 μm. Spectral grids consisting of 15 by 15 (225 total), 20 by 20 (400 total), and 100 by 100 (10,000 total) Raman spectra were generated. The lateral and horizontal motion was controlled using a motorized stage, and the height above the sample was held constant for all measurements.

Data collected using “high spectral” resolution were generated using typically 400 total Raman spectra (20 by 20 spectral grid) with 10 seconds of integration time and 3 co-averages. Using this methodology, the total analysis time is ~200 minutes. For “high spatial” resolution data, 10,000 total Raman spectra (100 by 100 spectral grid) were collected over the same area with typically 1 second of integration time and no co-averages. Using this methodology, the total analysis time is ~167 minutes. Furthermore, the “high spectral” resolution chemical maps and resolved spectra shown in this work were generated using 400 total Raman spectra (20 by 20 spectral grid) with integration times of 15 seconds. The “high spatial” chemical maps and resolved spectra shown in this work were generated using 10,000 total Raman spectra (100 by 100 spectral grid) with an integration time of 1 second and no co-averages. Data sets 1-15 were generated using “high spectral” resolution, and data sets 16-19 were generated using “high spatial” resolution.

Multivariate curve resolution-alternating least squares (MCR-ALS). MCR-ALS[23, 25, 27, 28] is used to resolve the spatial and spectral information about unique components that are imbedded in a hyperspectral image. A significant advantage of MCR-ALS is that prior information about the sample is not essential. MCR-ALS resolves an experimental data matrix, **D**, using:

$$\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{E} \quad (1)$$

where **C** is the concentration profile matrix of each chemical component, **S**^T is the resolved spectra matrix, and **E** is the error matrix. The number of components contributing to **D** can be determined by prior knowledge of the system, principal component analysis (PCA), or other multivariate techniques. The calculation and iterative optimization of **C** and **S**^T by ALS is subsequently performed after an initial estimation of **S**. Constraints of non-negative concentrations and non-negative spectral intensity are often employed during ALS to help guide solutions to the true value. Convergence is achieved by applying Eq. (2) and Eq. (3) in an alternating fashion to the updated estimates of **C** and **S**, denoted as **Ĉ** and **Ŝ**, respectively:

$$\hat{\mathbf{S}} = \mathbf{D}^T \hat{\mathbf{C}} / \hat{\mathbf{C}}^T \hat{\mathbf{C}} \quad (2)$$

$$\hat{\mathbf{C}} = \mathbf{D} \hat{\mathbf{S}} / \hat{\mathbf{S}}^T \hat{\mathbf{S}} \quad (3)$$

In the current study, MCR-ALS is applied to the experimental data matrix, **D**, containing the spatial and spectral information. Each row of **D** is the intensity at various wavenumbers. The number of components was selected prior to the ALS step using initial estimations from PCA. When the model derived from these initial estimations did not suffice, the number of components was optimized by comparison of the resolved spectra in **S** with Raman spectra of appropriate reference materials. Therefore, the number of selected components was increased until the resolved spectra were sufficiently comparable to the Raman spectra of respective reference materials. The MCR-ALS results

shown in this work were generated using twenty-component models. Initial estimates of spectra for ALS were determined by distance criteria, in which the first spectrum for initialization was selected to be furthest from the mean. Moreover, subsequent spectra were selected to be furthest from the mean and all prior selected samples. The constraints of non-negative concentration and non-negative spectral intensity were applied, and a 0.01% convergence was used.

All MCR-ALS results were generated in Matlab 7.12 (Mathworks) with the PLS toolbox (Eigenvector Research Inc.). The final concentration profile matrix, **C**, contains each chemical component's concentration profile, and each column in **C** thus corresponds to a component. Chemical maps are subsequently reconstructed from **C** using Matlab with the PLS Toolbox. OriginPro (Origin Lab v9.1 Pro) was used for visualization of the chemical maps, as shown in the respective MCR-ALS figures. The chemical maps are presented in terms of percent spectral contributions to investigate the relative magnitude of the chemical species within a sample. Furthermore, this percent spectral contribution is based on the chemically meaningful species within the sample. For example, if six chemically meaningful species are identified within a sample, each chemical map generated is the concentration matrix, **C**, of the respective chemical species divided by the summation of six total chemical species' concentration matrices. In the resolved spectra matrix, **S**, each row contains the resolved spectrum. The entire spectral range, 70-1550 cm^{-1} , was used for MCR-ALS analysis. No preprocessing was performed prior to analysis by MCR-ALS. The graphical representations of the individual spectra were generated using OriginPro.

Data, value and validation

The nineteen total data sets, directly provided in this work, are of Raman microspectroscopic mapping measurements collected on TiO_2 -II-bearing grains from the four spherule layers—CSL, JSL, MSL, and BGSL. Of the nineteen data sets, fifteen data sets are deemed “high spectral” resolution data and four are deemed “high spatial” resolution data. The “high spectral” resolution data are collected using typically 20 by 20 spectral grids with long integration times and co-averages. The “high spatial” resolution data are collected using 100 by 100 spectral grids with short integration times and no co-averages. Of the “high spectral” resolution data, one data set is of a CSL grain, two data sets are of a JSL grain, five data sets are of MSL grains, and seven data sets are of BGSL grains. Of the “high spatial” resolution data, one data set is of a JSL grain, two data sets are of MSL grains, and one data set is of a BGSL grain.

Each available data set is stored as a two-dimensional matrix. The columns of this matrix are the number of spectra collected—typically 400 total Raman spectra for the “high spectral” resolution data and 10,000 total Raman spectra for the “high spatial” resolution data—which correspond to the location of the collected Raman spectrum. The rows of this matrix are the spectral region—70 to 1550 cm^{-1} in increments of 0.5 cm^{-1} .

The Raman microspectroscopic mapping data presented here was validated in previous studies.[16, 26] Furthermore, the available data sets were validated by comparison of the measured Raman spectra—including the Raman band locations and spectral shapes—with both Raman spectra of reference materials and Raman spectra from the RRUFF database project.[29] Additionally, during Raman spectral acquisition, calibration of both the source wavelength and Raman shift are internally

performed using a neon lamp. Through this internal calibration, the accuracy of the resulting Raman spectra is confirmed.

A detailed description of the results presented in this work is given in the Supplemental Material. In brief, Raman microspectroscopy (**Figure 1**) and Raman microspectroscopic mapping (**Figures 2 and 3**) were used to investigate TiO₂-II-bearing grains recovered from the four spherule layers. Previous studies have documented TiO₂-II in 34 grains from the spherule layers[16] and provided detailed chemical imaging of selected grains[26]. In this work, the results from MCR-ALS applied to the Raman microspectroscopic mapping data of a selected MSL grain are presented. This MSL grain was analyzed using both “high spectral” (**Figure 2**) and “high spatial” (**Figure 3**) resolution Raman microspectroscopic mapping.

(Insert Figure 1 here)

The BSE image of the MSL grain reveals a heterogeneous sample with polydispersed micron- and submicron-sized and shaped particles. Raman spectra collected with both “high spectral” (**Figure 1B**) and “high spatial” (**Figure 1C**) resolution indicate the presence of rutile (**Figure 1B/C, spectra #1**), TiO₂-II (**Figure 1B/C, spectra #2**), quartz (**Figure 1B/C, spectra #4**), and substrate-adhesive epoxy (**Figure 1B/C, spectra #5**). The intensity of the 145 cm⁻¹ band (**Figure 1B/C, spectra #3**) suggests that anatase may also be present.

(Insert Figure 2 here)

Raman microspectroscopic mapping with MCR-ALS (**Figure 2**) collected on the MSL grain provided chemical maps, pixel-by-pixel chemical images, and resolved Raman spectra for the five distinct chemical species—rutile, TiO₂-II, anatase, quartz, and substrate-adhesive epoxy—that were resolved. This “high spectral” resolution mapping shows that rutile dominates the grain, and TiO₂-II is distributed in a complementary fashion to rutile. Moreover, anatase is localized, quartz is distributed largely on the outer portions of the grain, and substrate-adhesive epoxy is located exterior to the grain.

(Insert Figure 3 here)

MCR-ALS applied to Raman microspectroscopic mapping, collected with “high spatial” resolution (**Figure 3**), of the MSL grain provided chemical maps, pixel-by-pixel chemical images, and resolved Raman spectra for rutile, TiO₂-II, anatase, quartz, and substrate-adhesive epoxy. This “high spatial” resolution mapping provides a more refined distribution of these chemical species; however, given the limited spectral acquisition parameters, it is more difficult to spectrally resolve some minor chemical species, such as quartz.

The data in this work offers significant value to both the chemical and broader scientific community in several ways. First, the data offers the ability to develop and test diverse algorithms for image processing. Second, the data offers a comparison between high spectral and high spatial resolution chemical imaging, and therefore, provides the ability to pursue both data fusion of these two measurements for improved imaging capabilities and image enhancements for certain regions of

interest. Third, the data provides a vast resource for developing and testing multivariate analysis and chemometric methods. Specifically, with the data being comprised of three diverse TiO₂ polymorphs, it can serve as a textbook data set for the classification of TiO₂ polymorphs. Overall, this data provides a myriad of opportunities for the scientific community in wide ranging applications, including the chemical imaging and multivariate analysis disciplines.

Acknowledgments

The authors thank the National Science Foundation (Chem312184 and Career Grant 1352095) and the Delaware Space Grant College and Fellowship Program (NASA Grant NNX15A119H) for support of this research.

References

- [1] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D.D. Dionysiou, A Review on the Visible Light Active Titanium Dioxide Photocatalysts for Environmental Applications, *Appl. Catal., B*, 125 (2012) 331-349.
- [2] S.U.M. Khan, M. Al-Shahry, W.B. Ingler, Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂, *Science*, 297 (2002) 2243-2245.
- [3] K. Nakata, A. Fujishima, TiO₂ Photocatalysis: Design and Applications, *J. Photochem. Photobiol. C*, 13 (2012) 169-189.
- [4] G. Meinhold, Rutile and its Applications in Earth Sciences, *Earth-Sci. Rev.*, 102 (2010) 1-28.
- [5] T. Zhu, S.P. Gao, The Stability, Electronic Structure, and Optical Property of TiO₂ Polymorphs, *J. Phys. Chem. C*, 118 (2014) 11385-11396.
- [6] Y.C. Lan, Y.L. Lu, Z.F. Ren, Mini Review on Photocatalysis of Titanium Dioxide Nanoparticles and their Solar Applications, *Nano Energy*, 2 (2013) 1031-1045.
- [7] K. Spektor, D.T. Tran, K. Leinenweber, U. Häussermann, Transformation of Rutile to TiO₂-II in a High Pressure Hydrothermal Environment, *J. Solid State Chem.*, 206 (2013) 209-216.
- [8] S.L. Hwang, P.Y. Shen, H.T. Chu, T.F. Yui, Nanometer-Size Alpha-PbO₂-Type TiO₂ in Garnet: A Thermobarometer for Ultrahigh-Pressure Metamorphism, *Science*, 288 (2000) 321-324.
- [9] X.L. Wu, D.W. Meng, Y.J. Han, Alpha-PbO₂-type Nanophase of TiO₂ from Coesite-Bearing Eclogite in the Dabie Mountains, China, *Am. Mineral.*, 90 (2005) 1458-1461.
- [10] R. Wirth, F. Kaminsky, S. Matsyuk, A. Schreiber, Unusual Micro- and Nano-Inclusions in Diamonds from the Juina Area, Brazil, *Earth Planet. Sci. Lett.*, 286 (2009) 292-303.
- [11] L.F. Dobrzhinetskaya, R. Wirth, J.S. Yang, I.D. Hutcheon, P.K. Weber, H.W. Green, High-Pressure Highly Reduced Nitrides and Oxides from Chromitite of a Tibetan Ophiolite, *Proc. Natl. Acad. Sci. U.S.A.*, 106 (2009) 19233-19238.
- [12] A. El Goresy, M. Chen, P. Gillet, L. Dubrovinsky, G. Graup, R. Ahuja, A Natural Shock-Induced Dense Polymorph of Rutile with Alpha-PbO₂ Structure in the Suevite from the Ries Crater in Germany, *Earth. Planet. Sci. Lett.*, 192 (2001) 485-495.

- [13] J.C. Jackson, J.W. Horton, I.M. Chou, H.E. Belkin, A Shock-Induced Polymorph of Anatase and Rutile from the Chesapeake Bay Impact Structure, Virginia, USA, *Am. Mineral.*, 91 (2006) 604-608.
- [14] M. Chen, X.P. Gu, X.D. Xie, F. Yin, High-Pressure Polymorph of TiO_2 -II from the Xiuyan Crater of China, *Chin. Sci. Bull.*, 58 (2013) 4655-4662.
- [15] B.P. Glass, M. Fries, Micro-Raman Spectroscopic Study of Fine-Grained, Shock-Metamorphosed Rock Fragments from the Australasian Microtektite Layer, *Meteorit. Planet. Sci.*, 43 (2008) 1487-1496.
- [16] F.C. Smith, B.P. Glass, B.M. Simonson, J.P. Smith, A.E. Krull-Davatzen, K.S. Booksh, Shock-Metamorphosed Rutile Grains Containing the High-Pressure Polymorph TiO_2 -II in Four Neoproterozoic Spherule Layers, *Geology*, 44 (2016) 775-778.
- [17] S. Koljenovic, T.C.B. Schut, J.P. van Meerbeeck, A. Maat, S.A. Burgers, P.E. Zondervan, J.M. Kros, G.J. Puppels, Raman Microspectroscopic Mapping Studies of Human Bronchial Tissue, *J. Biomed. Opt.*, 9 (2004) 1187-1197.
- [18] P. Xu, J.M. Kang, J. Suhr, J.P. Smith, K.S. Booksh, B.Q. Wei, J.Y. Yu, F.X. Li, J.H. Byun, Y. Oh, T.W. Chou, Spatial Strain Variation of Graphene Films for Stretchable Electrodes, *Carbon*, 93 (2015) 620-624.
- [19] M. Lopez-Lopez, M.A.F. de la Ossa, C. Garcia-Ruiz, Fast Analysis of Complete Macroscopic Gunshot Residues on Substrates Using Raman Imaging, *Appl. Spectrosc.*, 69 (2015) 889-893.
- [20] J. Nallala, O. Piot, M.D. Diebold, C. Gobinet, O. Bouche, M. Manfait, G.D. Sockalingum, Infrared and Raman Imaging for Characterizing Complex Biological Materials: A Comparative Morpho-Spectroscopic Study of Colon Tissue, *Appl. Spectrosc.*, 68 (2014) 57-68.
- [21] X. Zhang, A. de Juan, R. Tauler, Multivariate Curve Resolution Applied to Hyperspectral Imaging Analysis of Chocolate Samples, *Appl. Spectrosc.*, 69 (2015) 993-1003.
- [22] C.M. Stellman, K.S. Booksh, A.R. Muroski, M.P. Nelson, M.L. Myrick, Principal Component Mapping Applied to Raman Microspectroscopy of Fiber-Reinforced Polymer Composites, *Sci. Eng. Compos. Mater.*, 7 (1998) 51-80.
- [23] M. Ando, H.O. Hamaguchi, Molecular Component Distribution Imaging of Living Cells by Multivariate Curve Resolution Analysis of Space-Resolved Raman Spectra, *J. Biomed. Opt.*, 19 (2014) 6.
- [24] B. Vajna, G. Patyi, Z. Nagy, A. Bodis, A. Farkas, G. Marosi, Comparison of Chemometric Methods in the Analysis of Pharmaceuticals with Hyperspectral Raman Imaging, *J. Raman Spectrosc.*, 42 (2011) 1977-1986.
- [25] J. Felten, H. Hall, J. Jaumot, R. Tauler, A. de Juan, A. Gorzsas, Vibrational Spectroscopic Image Analysis of Biological Material using Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS), *Nat. Protoc.*, 10 (2015) 217-240.
- [26] J.P. Smith, F.C. Smith, J. Ottaway, A.E. Krull-Davatzen, B.M. Simonson, B.P. Glass, K.S. Booksh, Raman Microspectroscopic Mapping with Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) Applied to the High-Pressure Polymorph of Titanium Dioxide, TiO_2 -II, *Appl. Spectrosc.*, (2016) In Press.
- [27] A. de Juan, J. Jaumot, R.A. Tauler, Multivariate Curve Resolution (MCR). Solving the Mixture Analysis Problem, *Anal. Methods*, 6 (2014) 4964-4976.
- [28] H. Motegi, Y. Tsuboi, A. Saga, T. Kagami, M. Inoue, H. Toki, O. Minowa, T. Noda, J. Kikuchi, Identification of Reliable Components in Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS): A Data-Driven Approach Across Metabolic Processes, *Sci. Rep.*, 5 (2015) 12.

[29] B. Lafuente, R.T. Downs, H. Yang, N. Stone, The Power of Databases: the RRUFF Project, in: T. Armbruster, R.M. Danisi (Eds.) *Highlights in Mineralogical Crystallography*, De Gruyter, Berlin, Germany, 2015, pp. 1-30.

Figures

Figure 1: Backscattered electron (BSE) image (A) of a selected MSL grain. Raman spectra acquired with high spectral resolution (B) were collected at the corresponding numbered locations shown in blue (A). Raman spectra acquired with high spatial resolution (C) were collected at the corresponding numbered locations shown in red (A).

Figure 2: Spatially-resolved chemical maps, spatially-resolved pixel-by-pixel chemical images, and resolved Raman spectra of rutile (B), TiO_2 -II (C), anatase (D), quartz (E), and substrate-adhesive epoxy

(F) generated using MCR-ALS applied to Raman microspectroscopic mapping. The backscattered electron (BSE) image (A), optical image (A), and mean spectrum (black, A) +/- the standard deviation (+ in red, - in blue; A) are shown. Raman microspectroscopic mapping results were generated using 532 nm excitation and a 20 by 20 spectral grid.

Figure 3: Spatially-resolved chemical maps, spatially-resolved pixel-by-pixel chemical images, and resolved Raman spectra of rutile (A), TiO₂-II (B), anatase (C), quartz (D), and substrate-adhesive epoxy (E) generated using MCR-ALS applied to Raman microspectroscopic mapping. Raman microspectroscopic mapping results were generated using 532 nm excitation and a 100 by 100 spectral grid.