Mineral quartz concentration measurements of mixed mineral dust/urban haze pollution plumes over Korea with multiwavelength aerosol Raman-quartz lidar

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[1] We present a case study of a concentration measurement of mineral quartz immersed in East Asian urban pollution. We use a novel lidar measurement technique that uses signals from Raman scattering from quartz at ultraviolet (360 nm) wavelength. The particle-extinction-related Ångström exponent (wavelength pair 355/532 nm) varies around 0.7 ± 0.2 , the lidar ratio is 50–55 sr at 532 nm. The numbers indicate that the pollution plume likely consisted of a mixture of mineral dust with urban haze. Dust concentrations vary between 8–11 $\mu g/cm^3$. We determined Raman quartz concentrations from measurements simultaneously carried out at 546 nm, which allows us to measure for the first time the Raman-quartz-related Ångström exponent of mineral dust. Values are 3–4, whereas we expect a theoretical value of 4. It is unclear if the lower values follow from retrieval uncertainties or if they are linked to the internal structure of the quartz grains. **Citation:** Müller, D., I. Mattis, B. Tatarov, Y. M. Noh, D. H. Shin, S. K. Shin, K. H. Lee, Y. J. Kim, and N. Sugimoto (2010), Mineral quartz concentration measurements of mixed mineral dust/urban haze pollution plumes over Korea with multiwavelength aerosol Raman-quartz lidar, *Geophys. Res. Lett.*, *37*, L20810, doi:10.1029/2010GL044633.

1. Introduction

[2] Dust has considerable influence on the Earth's radiative budget [*Schwartz and Andreae*, 2002]. Next to the Sahara, an equally important source of dust is Central Asia from where dust is transported over East Asia to the adjacent Pacific Ocean. In Asia the problem of dust in the atmosphere is much more severe than in other areas of the world, as dust often is mixed with urban haze. Scientific knowledge on the mixing state of dust with anthropogenic pollution is very limited. Satellite passive remote sensing for instance neither can separate the mixing state of urban haze from desert dust nor can it be used for an accurate positioning of mineral dust relative to another pollution layers or cloud layers.

[3] Thus there is strong need for measurement technologies that allow us to monitor the vertical distribution of mineral dust immersed in continental pollution plumes. *Tatarov and Sugimoto* [2005] show that the content of mineral quartz in a mixed urban/dust plume can be determined from measurements of the lidar return signals from Raman scattering from mineral quartz at 546 nm (quartz Raman line at 466 cm^{-1}), equivalent to a laser excitation wavelength at 532 nm. We apply this technology for the first time to the ultraviolet region. Using the ultraviolet region has the advantage that the scattering cross-section of mineral quartz is considerably higher compared to the visible wavelength range. Thus lower dust concentrations can be measured. Another advantage is that the ultraviolet wavelength is in the eye-safe region of the spectrum.

[4] In section 2 we describe the methodology. In section 3 we present a measurement example. We close our contribution in section 4 with a summary.

2. Methodology

[5] We collected data with our multiwavelength Raman lidar system at the Gwangju Institute of Science and Technology (GIST; 35.2° N, 126° E), Republic of Korea (South Korea). The instrument and the methodology used to derive profiles of particle backscatter coefficients at 355, 532, and 1064 nm, and extinction coefficients at 355 and 532 nm are described by *Noh et al.* [2007]. Particle extinction coefficients cannot be retrieved below approximately 700 m above ground because of the incomplete overlap between laser beam and telescope receiver field of view of our instrument. Profiles shown in this contribution were cut below heights for which the overlap affects data analysis.

[6] We measured the profile of the linear volume (particle plus molecule) depolarization ratio. It is defined as the ratio of the lidar signal perpendicularly polarized to the signal that is polarized parallel with respect to the polarization of the transmitted laser beam. The linear particle depolarization ratio follows according to the methods described by *Cairo et al.* [1999] and *Sakai et al.* [2002].

[7] From the backscatter and extinction coefficients we derive particle extinction-to-backscatter (lidar) ratios at 355 and 532 nm, the extinction-related Ångström exponents for the wavelength pair of 355/532 nm and the backscatter-related Ångström exponents for the wavelength pair of 355/532 nm and 532/1064 nm. In this contribution, we could not determine the backscatter-related Ångström exponents for the wavelength pair of 355/532 nm, because of detector problems of the channel that measures the elastic backscatter signals at 355 nm.

[8] We installed channels for inferring the mineral quartz concentration. The channels utilize the Raman return signals from silicon dioxide which is one main component of mineral quartz. The measurement technology is described by *Tatarov and Sugimoto* [2005] who use Raman return

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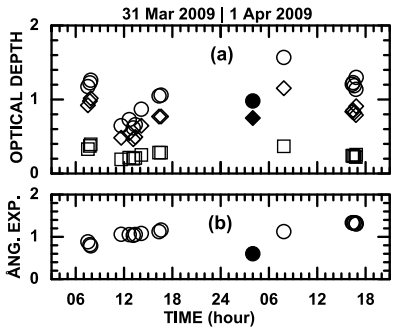

Figure 1. Time series of (a) particle optical depth measured with Sun photometer at 380 nm (circles), 500 nm (open diamonds) and 1020 nm (open boxes), and (b) the particle extinction Ångström exponent for the wavelength pair at 380/500 nm (circles). Also shown is optical depth (from ground to top of pollution layer) measured with lidar at 355 nm (bullet) and 532 nm (close diamond), and the Ångström exponent (from 700 m height to top of the pollution layer) for the wavelength pair at 355/532 nm (bullet). The measurement time was from 02:44–04:12 local time on 1 April. The data represent the conditions on 31 March and 1 April 2009.

signals at 546 nm. We operated for the first time a *Raman quartz channel* at 361 nm. Instrument setup, optical components, and details of the operation mode are described in the companion paper to this contribution (B. Tatarov et al., Lidar measurements of Raman scattering at ultraviolet wavelength from mineral dust over East Asia, submitted to *Optics Communications*, 2010).

3. Results

[9] Figure 1 shows the time series of particle optical depth and particle Ångström exponents measured on 31 March and 1 April 2009 with the AERONET Sun photometer [*Holben et al.*, 1998] that is operated at GIST. Optical depth varied between 0.5–1 at 500 nm and 0.6–1.6 at 380 nm. The column-mean extinction Ångström exponent varied around 1 in the evening of March 31 and in the morning hours of 1 April 2009.

[10] Figure 2 shows the extinction-related Ångström exponents from lidar. The column mean values varied around 0.6 ± 0.1 in the height range from 0.8–2 km on 31 March/1 April 2009. The Ångström exponents show that the haze layer likely did not consist of pure mineral dust. In such a case we expect values around zero [*Müller et al.*, 2010; *Tesche et al.*, 2009]. The backscatter-related Ångström exponent (wavelength pair 532/1064 nm) varies around 1.5 in the center of the mixed pollution plume (below 1.2 km height), and it increases to around 2 above that height range. Our retrievals are affected by large uncertainties. If we compare these numbers to results for pure mineral dust we find again that our values are larger. For pure mineral dust the backscatter-related Ångström exponent varies around 0.5 [*Tesche et al.*, 2009].

[11] Simulations with the Lagrangian particle dispersion model FLEXPART [*Stohl et al.*, 1998] also indicate that the pollution layers consisted of a mixture of urban haze with mineral dust. Mineral dust was transported from the Gobi desert in heights below 1–1.5 km. Along that track the dust plume passed over urbanized areas like Beijing in China and Seoul in Korea, which makes it highly likely that urban haze was mixed into the dust. Above around 1.5 km height there was little contribution from mineral dust in the pollution plume.

[12] Figure 2 shows that the haze layer extended to approximately 2 km height above ground level on 31 March/1 April 2009. We could not derive the particle backscatter coefficient at 355 nm for that measurement day because of detector problems of the 355 nm elastic channel. All other channels were functional during the measurement period. The extinction coefficient at 355 nm and the backscatter coefficient at 361 nm can be retrieved without using the 355 nm elastic signal.

[13] The integrated particle extinction profiles result in an optical depth of 0.75 at 532 and 0.98 at 355 nm. We computed optical depth from surface to 700 m altitude on the basis of the extinction value at 700 m and assuming that extinction is constant down to the ground. This assumption likely gives us only a lower limit of optical depth.

[14] The particle lidar ratios are around 50–55 sr at 532 nm. Measurements of mixed urban haze/Asian dust plumes over Tsukuba, Japan, usually show lidar ratios of 45–55 sr at 532 nm. *Sakai et al.* [2002] measured lidar ratios

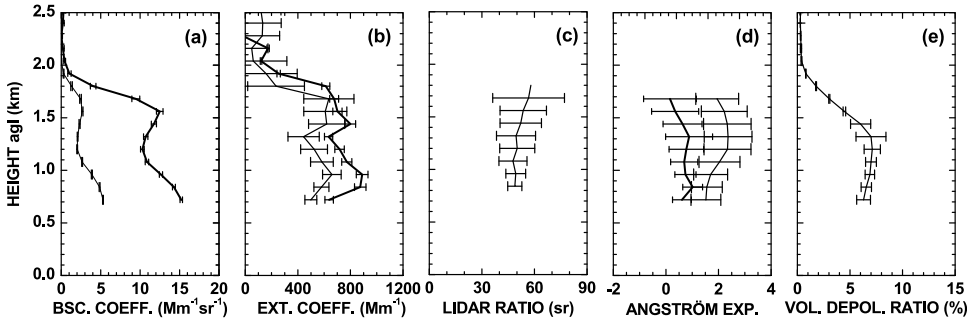

Figure 2. Profiles of (a) the particle backscatter coefficients at 532 (thick) and 1064 nm (thin), (b) the particle extinction coefficients at 355 (thick) and 532 nm (thin), (c) the particle lidar ratio at 532 nm, (d) the extinction-related Ångström exponents for the wavelength pair 355/532 nm (thick) and the backscatter-related Ångström exponent for the wavelength pair 532/1064 nm (thin), and (e) the linear volume (molecules + particles) depolarization ratio at 532 nm. The measurement time was from 02:44–04:12 local time on 1 April 2009. Error bars denote one-standard deviation, respectively; agl denotes height above ground level.

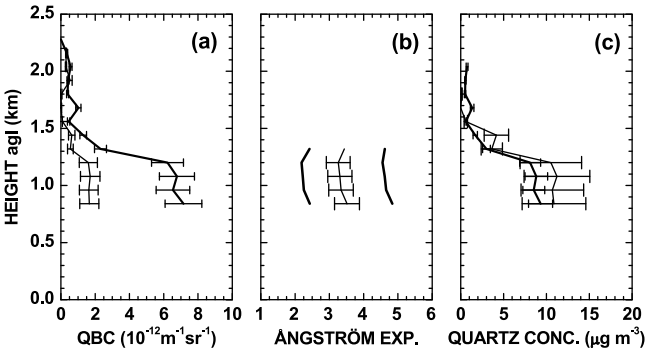

Figure 3. (a) Backscatter coefficients of mineral quartz measured at 361 nm (thick) and 546 nm (thin). The quartz Raman signal were collected from 23:27 LT (31 March 2009) to 2:27 LT (1 April 2010). Details on the method that was used to combine the signals with the nitrogen Raman signals are given by Tatarov et al. (submitted manuscript, 2010). (b) Raman quartz-backscatter related Ångström exponent (thin) calculated from the profiles in (a). Also shown are the extreme values of this Ångström exponent (thick without error bars). These profiles were computed by using the minimum (maximum) values of the 361-nm profile and the maximum (minimum) values of the 546-nm profile. (c) Profiles of the mineral quartz concentration derived from the quartz backscatter coefficients at 361 (thick) and 546 nm (thin). Error bars in Figures 3a–3c denote one-standard deviation.

of 46 sr ± 5 sr and *Murayama et al.* [2004] measured 43 sr ± 1 sr at 532 nm for mineral dust plumes observed over Japan. *Liu et al.* [2002] find lidar ratios of 51 ± 6 sr at 532 nm. *Noh et al.* [2008] measured a mean lidar ratio of 52 sr at 532 nm at GIST.

[15] The linear volume depolarization ratio varies around 5–8%. The elevated depolarization ratios indicate the presence of depolarizing mineral dust particles. The absolute values, however, may be incorrect. Our system still suffers from calibration uncertainties.

[16] Figure 3 shows the profiles of the quartz backscatter coefficients at 361 nm and 546 nm. Values larger than 0 show that mineral dust was present up to 1.2–1.5 km height. The error sources for the quartz retrievals are described by Tatarov et al. (submitted manuscript, 2010).

[17] The Raman quartz-backscatter-related Ångström exponent describes the wavelength dependence of the Raman scattering cross section of quartz. The mean profile varies around 3.5 in the dust plume. The uncertainty bars are rather high because of the comparably low intensity of the Raman quartz backscatter signals.

[18] From theoretical considerations we expect a value of 4 for this Ångström exponent. This wavelength dependence follows in a first approximation from the proportionality to $(\nu - \nu s)^4$. The parameter νs denotes the Raman shift which is different from the Rayleigh molecular scattering from nitrogen. The Rayleigh scattering is elastic and $\nu s = 0$, i.e., there is no Raman shift.

[19] The slight underestimation of our experimental values may have different reasons. The Raman scattering cross section for quartz depends on temperature and on the structure of the crystals. We cannot exclude that the cross section is affected by resonance absorption. At the present moment we do not know the impact of these factors on the Raman scattering cross section of quartz and its wavelength dependence for quartz in atmospheric mineral dust. One goal of our ongoing studies is to obtain information on the cross section of mineral dust.

[20] Instrument performance and other steps in lidar signal analysis may also affect the accuracy of the Raman quartz-backscatter-related Ångström exponent. Possible error sources are calibration of the signals, leaking of interference filters, and errors in the analysis of the nitrogen Raman channels, as for example a wrong assumption of the aerosol Ångström exponent and an erroneous overlap correction function. In our lidar data analysis we did not apply any overlap correction, and we assume that full overlap is reached above 700 height agl.

[21] Figure 3 shows the profiles of the mineral quartz concentration. The profiles were obtained from the profiles of the quartz-backscatter coefficient and the values of the Raman scattering cross section for quartz. The cross sections at both laser pumping wavelengths were determined by the use of the known cross-section at the pumping wavelength of 488 nm [*Schoen and Cummins*, 1971] and by accounting for the $(\nu - \nu s)^4$ scaling of the scattering.

[22] We find 8–11 μg/m^3 mineral quartz. For comparison *Tatarov and Sugimoto* [2005] measured on average 7–13 μg/m^3 for a dust event over Japan in 2005. We obtain a maximum inaccuracy of 30% of the quartz concentration. This uncertainty follows from the difference between the commonly used power −4 law and the Raman quartz-backscatter-related Ångström exponent of 3 to 4. This uncertainty also includes the measurement errors and uncertainties introduced by signal analysis.

[23] Measurements of PM-10 are done on a routine basis by the Korea Meteorological Administration (KMA) in Gwangju. The surface-level observations were 72–96 μg/m^3 on 31 March 2009. The concentration of silicates is

Table 1. Peak Values of Silicate Concentrations, and Column-Mean Values of Ångström Exponents and Height Range for Which This Column Mean Value is Given[a]

Date	Concentration (μg/m^3)	PM-10 (μg/m^3)	Ångström Exponent	Height Range (m)
31 Mar 2009	11	72–96 (51)	3.4 ± 0.1	700–1100
15 Mar 2010	20	45–310 (119)	4 ± 1	1900–2400
16 Mar 2010	15	91–129 (107)	4 ± 0.8	1300–3100
21 Mar 2010	5	36–64 (44)	3 ± 0.1	3800–4600
23 Mar 2010	25	78–176 (122)	3.1 ± 0.3	960–1800

[a]Also shown is the range (minimum and maximum during a 24-h observation period) of the PM-10 concentrations measured at the surface on the respective days. Numbers in brackets denote the mean value for the 24-h measurement period.

approximately 50% in East Asian dust plumes. This means we can double the dust concentration values we derived from our lidar observations. We also need to consider possible error sources in the in-situ sampling. For instance it is not clear in how much fog and/or coarse mode urban particles and/or local dust affect the accuracy of the PM-10 measurements. Another reason for the higher in-situ values may be an inhomogeneous mixture of the dust plume, and which may be responsible for generally larger dust concentrations near ground compared to the concentrations in the lofted pollution layers.

4. Summary

[24] We present a case study of profile measurements of the Raman-backscatter coefficient of mineral quartz at 361 nm wavelength and the Raman-quartz backscatter-related Ångström exponent of Asian mineral dust. The quartz was mixed in an East Asian urban-pollution plume. The ultraviolet wavelength has advantage over measurements at visible wavelengths as it gives a higher signal-to-noise ratio, and thus is more sensitive to lower concentrations of silicates in mixed pollution plumes. The ultraviolet wavelength furthermore allows for observations in the eye-safe region. We find moderate quartz concentrations of <11 $\mu g/cm^3$ above 1 km height.

[25] We carried out regular measurements (approximately two times per week) during the East Asian dust seasons in spring 2009 and 2010 and fall 2009. The limitations in laser power, detector misalignments and saturation effects make our data analysis extremely time consuming, particularly for the measurements in 2009. Table 1 summarizes our results for mineral quartz concentrations measured on 4 days in 2010. The mean values are given for heights where overlap effects and detector problems can be neglected. We find on average Ångström exponents between 3–4. Quartz concentrations were between 5 $\mu g/m^3$ and 25 $\mu g/m^3$ in the polluted boundary layer.

[26] We will upgrade our lidar with particle depolarization channels at 355 and 1064 nm. As shown by *Tesche et al.* [2009] measurements of this parameter at two wavelengths allows us to separate mineral dust from, e.g., biomass burning aerosols. If that separation of signals is done we may derive profiles of microphysical properties like particle size and volume concentration with inversion algorithms [*Müller et al.*, 1999]. We will be able to investigate East Asian haze layers in a more refined way than what is currently possible with multiwavelength Raman lidar.

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References

Cairo, F., G. D. Donfrancesco, A. Adriani, P. Lucio, and F. Federico (1999), Comparison of various linear depolarization parameters measured by lidar, *Appl. Opt.*, *38*, 4425–4432.

Holben, B. N., et al. (1998), AERONET—A federated instrument network and data archive for aerosol characterization, *Remote Sens. Environ.*, *66*, 1–16.

Liu, Z., N. Sugimoto, and T. Murayama (2002), Extinction-to-backscatter ratio of Asian dust observed with high-spectral-resolution lidar and Raman lidar, *Appl. Opt.*, *41*, 2760–2767.

Müller, D., U. Wandinger, and A. Ansmann (1999), Microphysical particle parameters from extinction and backscatter lidar data by inversion with regularization: Theory, *Appl. Opt.*, *38*, 2346–2357.

Müller, D., et al. (2010), Mineral dust observed with AERONET Sun photometer, Raman lidar, and in situ instruments during SAMUM 2006: Shape-independent particle properties, *J. Geophys. Res.*, *115*, D07202, doi:10.1029/2009JD012520.

Murayama, T., D. Müller, K. Wada, A. Shimizu, M. Sekiguchi, and T. Tsukamoto (2004), Characterization of Asian dust and Siberian smoke with multi-wavelength Raman lidar over Tokyo, Japan in spring 2003, *Geophys. Res. Lett.*, *31*, L23103, doi:10.1029/2004GL021105.

Noh, Y. M., Y. J. Kim, B. C. Choi, and T. Murayama (2007), Aerosol lidar characteristics measured by a multi-wavelength Raman lidar system at Anmyeon island, Korea, *Atmos. Environ.*, *68*, 316–319.

Noh, Y. M., Y. J. Kim, and D. Müller (2008), Seasonal characteristics of lidar ratios measured with a Raman lidar at Gwangju, Korea, in spring and autumn, *Atmos. Environ.*, *42*, 2208–2224.

Sakai, T., et al. (2002), Case study of Raman lidar measurements of Asian dust events in 2000 and 2001 at Nagoya and Tsukuba, Japan, *Atmos. Environ.*, *36*, 5479–5489.

Schoen, P. E., and H. Z. Cummins (1971), Absolute cross sections for Raman and Brillouin light scattering in quartz, in *Proceedings of Second International Conference on Light Scattering in Solids*, edited by M. Balkanski, p. 460, Flammarion, Paris.

Schwartz, S. E., and M. O. Andreae (2002), Uncertainty in climate change caused by aerosols, *272*, 1121–1122, doi:10.1126/science.272.5265.112.

Stohl, A., M. Hittenberger, and G. Wotawa (1998), Validation of the Lagrangian particle dispersion model FLEXPART against large scale tracer experiment data, *Atmos. Environ.*, *32*, 4245–4264.

Tatarov, B., and N. Sugimoto (2005), Estimation of quartz concentration in the tropospheric mineral aerosols using combined Raman and high-spectral-resolution lidars, *Opt. Lett.*, *30*, 3407–3409.

Tesche, M., et al. (2009), Vertical profiling of Saharan dust with Raman lidars and airborne HSRL in southern Morocco during SAMUM, *Tellus, Ser. B*, *61*, 144–164.

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