4.3 Chemical Analysis of Aerosols in Mountain Regions

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1. Prologue: Why do we climb mountains?

The question "Why do people climb mountains?" has been asked since time immemorial. The answers given by mountain climbers are "because it's there" (George Mallory) or "because that's where the gods live" (Joji Habu in the Japanese movie *Summit of the Gods*).

In Japan, Buddhist associations known as Ko became popular during the Edo period (1603-1868), and pilgrimages to shrines on Mt. Fuji and visits to the great mountain were carried out frequently as a form of religious practice. Today, mountain climbing has become quite popular among middle-aged to elderly individuals and particularly among women, who have thereby earned the moniker "mountain girls." As of 2014, the population of mountain climbers in Japan was 8.6 million, the majority of whom engaged in recreational mountain climbing. Approximately 40% of these mountain climbers were aged 60 or over and cited improving health as their primary motivation.

When you climb a mountain, you free yourself from the tumult of the city. The air tastes sweet, and you feel the urge to take deep breaths. This leads to the question, what substances are contained in mountain air? The major gases that make up air in the mountains are no different than those at lower elevations. The higher up you go, the lower the atmospheric pressure and the thinner the air. Go too high and you can become oxygen deprived and develop altitude sickness. The atmospheric pressure at the top of Mt. Fuji is approximately 2/3 that at sea level.

What, then, is the composition and concentrations of air pollutants? Is it okay to breathe deeply at the top of a mountain? Actually, it is not clear how clean mountain air is compared with air at lower elevations. Air pollutants are not continuously monitored in the mountains as they are at the surface. Why do we need to climb mountains to study the air, especially since no one lives there? Why do we need to study the chemical composition of aerosols in mountain air? What do we already know at this point? We hope to answer these questions while introducing aerosol monitoring on Mt. Fuji.

2. Mountains are where clouds are formed

One major difference between mountain air and surface air is the presence of clouds. Complex airflow occurs on mountain slopes, resulting in continuous formation of clouds. On Mt. Fuji and other tall mountains, different types of clouds can be seen in different seasons. As described by the line "peeking its head above the clouds" in the children's song Fuji-no-Yama (Mt. Fuji), if you are looking down from the top of Mt. Fuji on a clear summer day, you might very well see a vast sea of clouds. Look at Mt. Fuji from below, you might see a Mt. Fuji whose top is covered by a cloud umbrella (cap cloud) with elliptical- or wing-shaped clouds (lenticular clouds) a little ways from the top on the downwind side. Mountains are places where clouds are continuously born (Fig. 4.3-1).

Fig. 4.3-1: Monitoring aerosols (PM2.5 fine particulate matter) at the top of Mt. Fuji. Many different types of clouds can be seen from the top

3. Clouds (fog) are not gas

Clouds that are in contact with the ground are called fog. What a mountain climber sees as fog, when seen from below, is a cloud. There is no clear distinction between clouds and fog.

When Japanese mountain climbers encounter clouds (or fog) and their visibility is hindered, they often say "it's getting gassy out.' Clouds are water vapor that has cooled and condensed to form water droplets (liquid). It is not gas. "It's getting cloudy" or "it's getting foggy" would be more scientifically correct.

The expression "getting gassy" is used only in the context of mountain climbing. Perhaps it comes from the image of white wisps of yuge (steam) coming from a kettle. Steam is water droplets that have formed when water vapor cools in the air. The first Chinese character in the word yuge is the same character used for kitai (gas), so perhaps someone misunderstood yuge to be the same as kitai.

That said, do clouds form spontaneously whenever there is water vapor? No. Dust particles (aerosols) have to be present to form the nuclei of cloud droplets.

4. Aerosols make clouds

Aerosols are minute solid or liquid particles ranging from 0.03 to 100 μm in size and suspended in air. The smallest objects that can be seen with the naked eye are about 100 μm (0.1 mm), so it is not possible to see aerosols. That said, particles greater than 10 μm readily settle due to gravity. The aerosols that are carried by upward currents to higher altitudes and create clouds are relatively small, measuring several micrometers in diameter. Cloud droplets are formed when water vapor condenses on such aerosols. Cloud droplets are around 10 μm (0.01 mm) in diameter. Although they technically fall into the aerosol category, they are differentiated from other aerosols. Incidentally, the rain droplets that form when cloud droplets collide with each other are approximately 1 mm in diameter.

It is important to know not only the size and number of aerosols but also their composition. For this reason, it is necessary to perform chemical analysis of the aerosols. The chemical composition of aerosols has a substantial impact on the chemical composition of cloud droplets. Aerosols comprising water-absorbing (hygroscopic) substances readily create water droplets. Such aerosols are referred to as condensation nuclei. However, not all condensation nuclei result in the formation of cloud droplets. Condensation nuclei that grow to the size of cloud droplets are known as cloud condensation nuclei (CCN). The most common cloud condensation nuclei are sea salt particles, which are created by the evaporation of sea spray, and sulfate aerosols, which are formed through the oxidation of sulfur dioxide in the atmosphere. Sulfate aerosols are the primary component of PM2.5.

5. Why do we study the chemical composition of mountain air?

Of Japan's total land area, 70% is mountainous and 67% is covered by forest. Although there is some variation by climatic division, all mountains except high mountains are covered by forests. For example, the timberline in the Central Alps and on Mt. Fuji is about 2500 m; thus, the lower mountains are almost entirely covered by forest. Forest makes the air that is essential for human life and also stores and purifies the water that serves as our drinking water.

One reason for studying mountain air is because if mountain air becomes polluted, then forest ecosystems may collapse. When forest ecosystems collapse, the water-holding capacity declines and rainwater flows over the ground surface, increasing the possibility of landslides and flooding. In Japan, reports of fir and Japanese beech tree degradation, particularly in mountainous areas, increased from the latter half of the 1980s into the 1990s. To determine the cause, efforts were begun in earnest to monitor air pollution in mountains near urban areas. Since the late 1980s, a group of researchers at Kanagawa University has been conducting long-term monitoring of air pollution, collecting data on gas, aerosol, fog, and rain on Mt. Oyama in the Tanzawa mountain range (Kanagawa Prefecture) (Igawa and Okochi, 2009).

Other reasons for studying mountain air quality are to monitor air pollution at the global scale, rapidly identify changes in air quality, and predict and develop responses to the future global environment. Air above 2000 m typically is not directly affected by the Earth's surface and is referred to as the free troposphere. Air in the free troposphere is relatively clean compared with air near the surface and can be used to study air quality at the global scale. There is nothing in the free troposphere to obstruct the flow of air. As such, winds in the free troposphere are characteristically strong. Pollutants that are transported to the free troposphere spread around the entire globe. High-altitude air sampling is carried out using airplanes. However, given the high cost of airplanes, such monitoring cannot be conducted continuously. This is where high mountains can be used to study the air quality in the free troposphere. Mt. Fuji is the highest peak in Japan and is the most suitable site for investigating the air quality in the free troposphere.

6. Mt. Fuji as a site for monitoring global air quality

Mt. Fuji is located at 35°N latitude, and its top is in the free troposphere. Mt. Fuji is located at the point where air pollutants exit Asia and are transported to the Pacific, so it is an ideal location for monitoring intercontinental transport between Asia and North America. At the same time, Mt. Fuji is located at the entry point of clean oceanic air and allows monitoring of the background concentrations of chemicals in Asia.

By virtue of its unique shape, Mt. Fuji enables researchers to not only monitor global air quality but also to conduct vertical monitoring. For example, Mt. Fuji provides an opportunity to study the transport of air pollutants from the ground surface to the free troposphere by monitoring rising air currents on summer days, to study in- and below-cloud scavenging of atmospheric pollutants, and to study the photochemical reactions in aqueous-phase at cloud tops that are subject to intense ultra-violet radiation.

7. Characteristics of summer aerosols on Mt. Fuji

Figure 4.3-2 shows the concentrations and relative proportions of nitrate and sulfate in aerosols and their precursors, namely nitric acid and sulfur dioxide in the gas phase, measured at the top of Mt. Fuji (3776 m) and at Tarobo (approx. 1300 m) near the Gotemba Trail at the southeastern foot of Mt. Fuji during the summer monitoring campaign in July and August. Total inorganic sulfur (sulfate and sulfur dioxide) tended to be higher both at the top and the foot of Mt. Fuji. Concentrations of both total inorganic nitrate (nitrate and nitric acid) and total inorganic sulfur at the top were approximately 2/5 of those at the foot.

The relative proportions of total inorganic nitrate present as aerosols (NO_3^-) and gas (HNO_3) were essentially the same at the top and at the foot. In contrast, the relative proportions of total inorganic sulfur differed between at the top and at the foot, with gaseous compounds (SO_2) dominating over aerosols (SO_4^{2-}) at the top and the reverse being true at the foot. The sulfate observed at the top represents sulfate that have undergone long-distance transport. Thus, we would expect SO_2 to have been oxidized to SO_4^{2-}. It is a mystery why SO_2 is being transported to Mt. Fuji without oxidation to SO_4^{2-}.

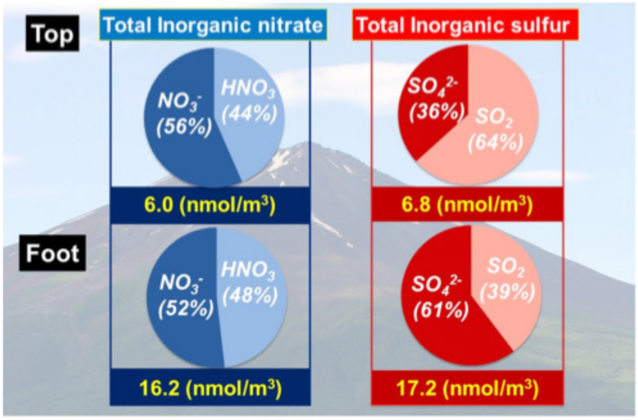


Fig. 4.3-2: Concentration of total inorganic nitrate and sulfur, and their relative proportions of gas and aerosols at the top and the southeastern foot of Mt. Fuji (2009-2015)

Figure 4.3-3 shows the relationship between concentration of nitrate/nitric acid and sulfate/sulfur dioxide and the direction of air mass, from which they were transported to the top of Mt. Fuji. The average concentrations of nitrate/nitric acid and sulfate/sulfur dioxide are shown for each of the 3 air masses by which they were transported to the top: oceanic, continental north, and continental south. It can be seen that the concentrations of nitrate/nitric acid and sulfate/sulfur dioxide are low when air mass is transported by ocean. In contrast, when the air mass is transported by the continent (both north and south), the concentrations of nitrate/nitric acid and sulfate/sulfur dioxide are high. Although the sample numbers are small, it appears that concentrations are the highest and that the proportion of sulfate is higher than that of sulfur dioxide when air comes from the continental north. As is evident from the above, the concentrations and composition of aerosols and gases differ according to the origin of the air mass, by which they were transported.

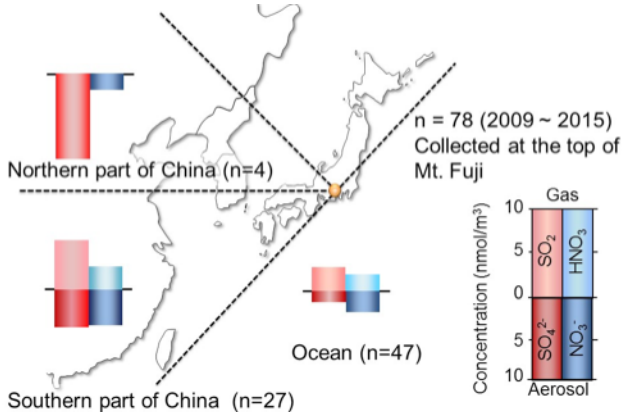
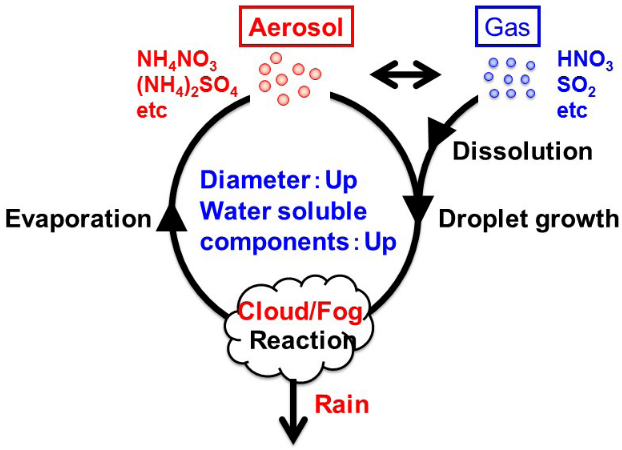


Fig. 4.3-3: Relationship between the concentrations of nitrate and sulfate in aerosols and their precursors, nitric acid and sulfur dioxide in the gas phase, at the top of Mt. Fuji and direction of air mass (2009-2015)



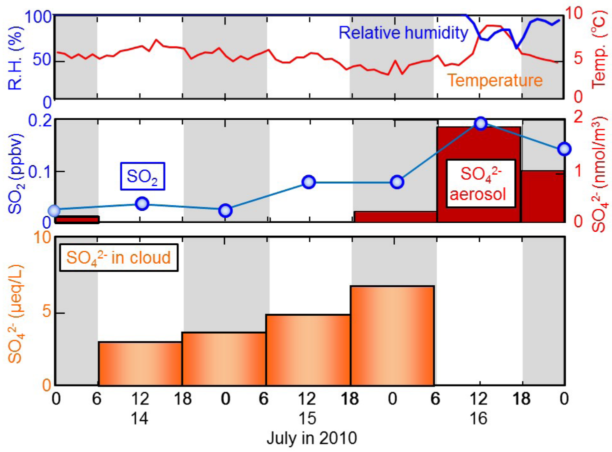


Fig. 4.3-4: Change in the concentration of sulfur dioxide in gas and of sulfate in aerosols and cloud water at the top of Mt. Fuji during 14-16 July in 2010

8. Gas-aerosol-cloud interactions

Cloud droplets that form on aerosol as CCN can absorb gases. The absorbed gases can react within cloud droplets and form new aerosols when cloud disappears. These new aerosols again become CCN for the formation of cloud droplets. This cycle is referred to as the gas-aerosol-cloud interaction. It is through this cycle that the air quality changes and cloud droplets fall to the ground when they grow to the size of rain droplets. This process helps to remove atmospheric contaminants and is known as precipitation scavenging.

Although this gas-aerosol-cloud interaction cannot be observed at low elevations, it could be observed at the top of Mt. Fuji, where clouds are frequently formed. Figure 4.3-4 shows the change of the concentration of sulfate and sulfur dioxide (middle panel in Fig. 4.3-4) and cloud water (bottom panel) collected at the same time at the top of Mt. Fuji. It is evident that sulfate is little detected in the presence of clouds and that the concentration of sulfate increases dramatically when the temperature rises and clouds disappear.

9. Conclusions

This paper explains the chemical composition of aerosols, focusing on transboundary air pollution and the cloud-forming ability of aerosols from the standpoint of chemical reactions. In terms of climate change, aerosols have the effect of warming or cooling the Earth depending on their composition (direct effects) and by forming clouds and increasing the amount of reflected sunlight (indirect effects). These effects are not mentioned in this paper but are discussed in others. We hope that you will take the time to read them together.