Oxygen and nitrogen isotopic constraints to the origin of saltpetre in historic gunpowder prevailed during the 19th century in Japan

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ABSTRACT

Saltpetre (KNO_3) is the major ingredient of gunpowder, which played a driving force in political changes during the late medieval to middle modern times in the world. The intrinsic isotopic parameters of the mineral are useful for elucidating the origin and following its marketing route. Dual isotopic analysis (oxygen together with nitrogen, as expressed by $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ notations, respectively) was made for nitrates from diverse gunpowder samples which prevailed during the 19th century in Japan. Three distinctive sources which represent Japanese domestic (characterized by low $\delta^{18}\text{O}$ - low $\delta^{15}\text{N}$ values), British Indian (characterized by clearly higher $\delta^{18}\text{O}$ - higher $\delta^{15}\text{N}$ values) and Atacama Desert nitrates (characterized by very high $\delta^{18}\text{O}$ up to +50 ‰ - $\delta^{15}\text{N}$ = around 0 ‰) were determined by binary plotting. Some samples recovered from portable powder reservoirs for less developed guns tend to exhibit a small shift in $\delta^{15}\text{N}$ value toward a British Indian origin, reflecting the positive mixing of the imported source

saltpetre from British Indian during preparation. Very unique gunpowder was discovered from the powder reservoirs for early models of the Enfield rifle in northeastern (Kiyokawa Village and Tsuruoka City in Yamagata Prefecture) and southwestern Japan (Miyoshi City in the inland of Hiroshima Prefecture) and metallic cartridges applicable to Lefauchaux and Smith & Wesson revolvers, all fall close to the alley of nitrates converted from the Atacama Desert nitrate formed by non-mass-dependent fractionation mixed with varying amounts of the British Indian nitrates. The evidence implies the prevalence of a unique marketing route. The saltpetre represents industrial conversion of the Atacama Desert nitrate (NaNO_3) by reaction with the mined potassium chloride in the middle 19th to early 20th centuries in Prussia (northern territory of Germany) and Great Britain. Dual isotopic analysis for nitrate in historic gunpowder provides direct evidence for the origin and subsequent marketing route during the 19th century in Japan. Socio-historic consequences of the use of Atacama Desert nitrate in manufacturing the gunpowder are reviewed and discussed, basing on the old documents.

1. Introduction

Saltpetre (KNO_3) constitutes one of the major ingredients of gunpowder (approximate proportion of saltpetre: native sulphur: charcoal=70:15:15 by weight). Since the first discovery in medieval China, gunpowder has been played a driving force during the political changes all over the world. Elucidation for the intrinsic origin of gunpowder employed in various conflicts and following its marketing route is a prerequisite for understanding the establishment of the socio-historical regimes.

Stable isotopic approaches provide firm evidence for better understanding these subjects. Nitrogen isotopic analysis, $^{15}\text{N}/^{14}\text{N}$ ratios as expressed by $\delta^{15}\text{N}$ notation, per mill variation relative to the atmospheric dinitrogen ($\delta^{15}\text{N} = 0 \text{ ‰}$) for nitrate in combination with socio-economic studies had recently been conducted (Mizota and Yamanaka, 2014, 2015; Mizota et al., 2014, 2015). Japanese domestic and British Indian origins were argued on the bases of the unique $\delta^{15}\text{N}$ values, since the values reflect the variations in the nitrogen sources from which nitrate is formed by microbial mineralization following by nitrification under diverse microbial activity.

The $\delta^{15}\text{N}$ values of nitrate are not the sole key to trace the origin. Another potential tool for better understanding the origin is the combined use (dual isotopic analysis) of $^{18}\text{O}/^{16}\text{O}$ ratios (as commonly designated by $\delta^{18}\text{O}$ notation, per mill variation relative to Standard Mean Ocean Water, SMOW) with $\delta^{15}\text{N}$ values (Kendall, 1998). This approach has increasingly been recognized in interdisciplinary studies such as atmospheric science, soil science, forensic

science, hydrology, geochemistry and marine ecological systems of upwelling areas (i.e., Michalski et al., 2010). Post-formational isotopic exchange with ambient water is known to be very limited, providing diverse applications for isotopic ratios (Kaneko and Poulson, 2013).

Two plausible origins, i.e., microbial vs. meteoric precipitation for nitrates in industrial saltpetre could be discriminated on the basis of the binary plotting of $\delta^{18}\text{O}$ value against $\delta^{15}\text{N}$ value (Kendall, 1998). During microbial oxidation of ammonium (NH_4^+) into nitrates (NO_3^-), among three oxygen atoms in nitrates, one oxygen atom is derived from atmospheric dioxygen, whereas the two others are derived from ambient water (Kendall, 1998). Atmospheric dioxygen has fairly constant $\delta^{18}\text{O}$ values of +23.5 ‰ over diverse ranges in the terrestrial environments (Spoelstra et al., 2007). Recent development in dual isotopic measurement for oxygen and nitrogen isotopic composition of nitrate can be made, using the denitrification method (Sigman et al., 2001; Casciotti et al., 2002). From the calculation of a simple binary mixing model, resulting oxygen isotopic composition of ambient water responsible for N-O bonding can be calculated (Böhlke et al., 1997). Then, the values were evaluated with respect to those of average ambient water under these environments to verify the origin. Nevertheless, such traditional interpretation has not been tested for saltpetre from historic gunpowder.

Another plausible source of nitrates in the industrial saltpetre involves the atmospheric origin formed by NO_x with ozone under non-mass-dependent fractionation (Michalski et al., 2004). Such nitrates represent NaNO_3 deposited in arid environments, as well known from Southern and Northern America (Böhlke et al., 1997), China (Qin et al., 2012) and Antarctica (Michalski et al., 2005). Since the discovery and subsequent exploitation of nitratine (NaNO_3) deposits in the early to middle 19th century, economic-sized deposits occurring in the inland desert areas of South America (Peru, Chile and Bolivia) have been used for chemical fertilizer and other industrial resources including gunpowder. The nitrates show unique $\delta^{18}\text{O}$ (up to +50 ‰) and $\delta^{15}\text{N}$ (around 0 ‰) values (Böhlke et al., 1997). Some gunpowder recovered from a given type of propellants showed unique $\delta^{15}\text{N}$ values of nitrates close to the atmospheric origin (Mizota and Yamanaka, 2014a). Such values implied the use of nitrates, which are commercially converted from nitrate ores of atmospheric origin by replacing Na with K ions. To verify the proposed interpretation, oxygen isotopic analysis for nitrates in gunpowder from the “conversion saltpetre” (Travis, 2014) prevailed during the middle to late 19th century is required.

The objective of the present study is to trace the genetic origin of saltpetre in historic gunpowder prevailing during the middle to late 19th century in Japan, using dual isotopic analysis. First, three end-members of the origin (Japanese domestic, British Indian and Atacama Desert nitrate) were settled. Then, analytical data for nitrate in diverse historic gunpowder were evaluated by referring to a database. Emphasis was placed on the unique saltpetre, which is

transformed from Atacama Desert nitrate. To verify the isotopic results, extensive historic documents directly relevant to the production of saltpetre in local and world-wide markets were examined.

2. Materials and methods

2.1. Description of the specimens examined

Seven historic saltpetre samples with high purity were collected from the inland areas of Gokayama Village (Fig. 1; southern Toyama, Prefecture), which were prepared during the late 19th century in central Japan, using the classic biotechnology. Another two specimens of high grade saltpetre were prepared from the crude aggregates grown on the clay floor under the current production of the indigo dye in Kamiita Town (Fig. 1; Tokushima Prefecture). The purification was made in the chemistry laboratory of Okayama University (Japan) in late April, 2015, using three repetitions of the differential crystallization following classic manuals (Itagaki, 2002). Details on the crystallization of these saltpetres formed by microbial nitrification will be reported elsewhere.

Four high grade and one rough saltpetre specimens of British Indian origin (Mizota et al., 2015) obtained from the Natural History Museum (London, The United Kingdom) and the Nagasaki Prefectural Tsushima Museum of History and Folklore (Izuhara, Tsushima, Japan) were involved.

The gunpowder samples analyzed in the present study are shown in Tables 1a and b. The gunpowder was recovered from bullets or portable powder reservoir, which had been handed down from generation to generation in Japan. The gunpowder samples were classified into two categories, according to the stylistics. Category 1 involves the gunpowder recovered from the portable powder reservoir, whereas category 2 represents samples from paper and metallic cartridges. From their stylistic evidence, category 1 is less developed; relative to those from category 2, which is more developed (Mizota et al., 2014). All the samples had been kept under dry conditions prior to the isotopic analysis, except for three samples from Tabaruzaka, Kumamoto, which were excavated from the soils in the battle field occurred at Civil War on March 1877. Up to the discovery probably around 1990, the iron-made bullets had been under burial conditions.

Relevant descriptions of all the gunpowder examined in the present study are shown in our previous articles (Mizota and Yamanaka, 2014, 2015; Mizota et al., 2014). Additional samples are three from Hagi City (Yamaguchi Prefecture) which were taken out from the copper cartridges applicable to Smith & Wesson .32 revolvers.

During the on-going analysis in the present study, additional acquisition and analysis of nitrates with atmospheric origin, i.e., meteoric precipitation and subsequent accumulation in extremely dry desert, were required. Table 1c involves the brief description of the Prussian saltpetre, three historic nitratine ore and four commercial sodium nitre, all intrinsic to Atacama Desert nitrate. A high-grade saltpetre specimen (Fig. 2; NSM-MF 00703) kept at the National Museum of Nature and Science (Ueno, Tokyo, Japan) with a label of the locality of the acquisition in Mayen, Rheinland, Prussia represents the specimen of German (*Prussian*) saltpetre (Guttman, 1895).

Historical documents kept in the custom house at Nagasaki harbor, Japan (present-day Nagasaki Museum of History and Culture; Document number (B 16 5-2) were examined for records of gunpowder and saltpetre importation in 1868.

2.2. Analytical methods

Depending on the concentration of nitrate-nitrogen, about 400 μg (nearly pure saltpetre) to 5 mg (low grade gunpowder) of dry powder was extracted by 10 ml of pure water in a plastic tube. Addition of one drop of ethanol followed by agitation with sonic waves was made to agitate the dissolution of saltpetre in the gunpowder. The extract was passed through a Millipore filter with a pore size of 0.20 μm .

The $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ were then measured according to the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Briefly, NO_3^- in a sample solution was quantitatively converted to nitrous oxide (N_2O) by denitrifying bacteria that lack N_2O -reductase activity. The N_2O was stripped from the sample vial using helium (He) as a carrier gas, purified by cryogenic trapping (Thermo Fisher Precon System), separated chromatographically (Thermo Fisher Gas Bench), and analyzed by mass spectrometry (Thermo Fisher Delta V Advantage). The ratios of $^{15}\text{N}:^{14}\text{N}$ and $^{18}\text{O}:^{16}\text{O}$ were expressed relative to atmospheric nitrogen for nitrogen and Vienna Standard Mean Ocean Water (V-SMOW) for oxygen. Isotope values were calibrated using the United States Geological Survey (USGS) and International Atomic Energy Agency (IAEA) internationally recognized nitrate standards: USGS-34, USGS-35, and IAEA-N3. Based on the replicate measurements of standards and samples ($n=120$), the analytical precisions for $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ were better than $\pm 0.2\text{‰}$ and $\pm 0.3\text{‰}$, respectively.

3. Results and discussion

3.1. Oxygen and nitrogen isotopic composition of three end-member saltpetre

As already described in the previous sections, it is highly plausible that three-end-member

saltpetre is involved in the ingredients of gunpowder which prevailed during the 19th century in Japan. Fig 3a shows the binary plotting for oxygen and nitrogen isotopic composition of the Japanese domestic (1 and 2), the British Indian saltpetre, the Atacama Desert nitrates and a Prussian saltpetre. Their spatial resolution is reasonably clear, indicating a useful database for discriminating nitrate with enough resolution by mass spectrometry. The former two $\delta^{15}\text{N}$ end-members represent microbial products formed under normal (Japanese domestic saltpetre 1) and higher temperatures (Japanese domestic saltpetre 2 and British Indian saltpetre). The Japanese domestic saltpetre 1 shows the $\delta^{18}\text{O}$ values ranging from +1.0 to +3.0 ‰ and $\delta^{15}\text{N}$ values from +4.1 to +5.0 ‰, whereas the corresponding figures for the Japanese saltpetre 2 are from +2.9 to +3.0 and from +8.2 to +8.6 ‰, respectively. The calculated $\delta^{18}\text{O}$ values of the ambient waters based on model calculation as described by Böhlke et al. (1997), are well consistent with those of the estimated soil waters from the relevant areas. Details will be published on our forthcoming paper. Nitrogen isotopic shifts of the saltpetre 1 toward higher $\delta^{15}\text{N}$ values, up to 4 ‰, as observed for the Japanese domestic saltpetre 2 result from the nitrification of residual NH_4^+ (with higher $\delta^{15}\text{N}$ values) released during the decaying process of the floral organic nitrogen (*Percicaria tinctoria*). Microbial saltpetre from the British Indian origin involves both rough and refined nitre (Mizota et al., 2015). Relative to the Japanese domestic saltpetre 1 and 2, distinctively higher $\delta^{18}\text{O}$ (+6.1 ~+7.3 ‰) and $\delta^{15}\text{N}$ (+12.3 ~+14.4 ‰) values are observable, reflecting the prevailing conditions of nitrification under intensive evaporation of soil water and organic origin of human and animal excreta with higher initial $\delta^{15}\text{N}$ values under huge demographic resources and feeding of a large number of domestic animals especially in Orissa and in the Ganga Valley. Surface soils are impregnated with potassium nitrate in a natural state (Mizota et al., 2015).

Atacama Desert nitrate shows distinctive $\delta^{18}\text{O}$ (+35.6 ~+50.4 ‰) and $\delta^{15}\text{N}$ (-4.8 ~+4.2 ‰) values (Böhlke et al., 1997) that result from the reaction of NO_x and ozone under non-mass-dependent fractionation (Michalski et al., 2004). Nitrates in a Prussian saltpetre (th144), three nitratine ores (th145, 146 and 147) and four, highly purified sodium niter (th118, 119, 142 and 143) analyzed in the present study were also plotted in the comparable region, all plotted in or nearby the region of Atacama Desert nitrate. The isotopic analysis of the th144 specimen reinforces the validity of the record on label (Fig. 2) as shown by the Prussian saltpetre. Table 1c also involves chemical composition of the unique saltpetre. High K (42.5 %) associated with high nitrate-nitrogen (13.2%) concentrations, relative to the calculated reagent grade KNO_3 specimen (K=38.6 %; nitrate-nitrogen=13.9 %) imply its high purity. No information is available on the natural deposits of the desert nitrates in Germany. Therefore, the unique nitrate might have transported from other regions. Further acquisition of comparable specimen with the historic Prussian saltpetre in known local museum or institution from the

western European countries involving Germany and neighboring countries was tried. Nevertheless, there could not be found any saltpetre with comparable origin. Historic consequence and relevant information of the unique saltpetre production in Germany is discussed in the later section.

Three additional nitratine ores and four recent commodity of sodium nitrate fertilizer showed somewhat higher $\delta^{18}\text{O}$ values in ranges from +52.0 to +54.7 ‰, but nearly the identical values of $\delta^{15}\text{N}$ values (-0.2 to +1.2 ‰), as compared with the previous analytical data by Böhlke et al. (1997). Whether such an observed small difference derives from heterogeneous nature of source ores or other reasons is not clear. Concentration of nitrate-nitrogen in three rough nitratine ores is low in range from 2.9 to 9.5 %.

3.2. Analysis of the historic gunpowder (Tables 1a, b)

Mechanics of explosives quickly developed through increased demands during the middle to late 19th century in Japan (Mizota et al., 2014). Various types of bullets were developed and prevailed in the world gun market. Dual isotopic analysis for nitrate recovered from the diverse types of gunpowder was made. The types of gunpowder were classified into two categories, according to stylistic evidence of the host guns. Category 1 (Fig. 3b) consists of gunpowder applicable to less evolved guns, whereas those of the category 2 (Fig. 3c) represent highly developed types consisting of paper or metallic cartridges applicable to breech-loading systems. Most gunpowder samples classified as category 1 show $\delta^{18}\text{O}$ - $\delta^{15}\text{N}$ values nearly comparable to those of Japanese domestic saltpetre 1 and 2 (Fig. 3a) or slightly shifted toward increased $\delta^{15}\text{N}$ values, all falling in the region of microbial origin of the nitrate (Böhlke et al., 1997). The $\delta^{15}\text{N}_{\text{nitrate}}$ values ranged from -0.3 to +11.7 ‰, where the concomitant $\delta^{18}\text{O}_{\text{nitrate}}$ showed more variable ranges from +2.9 to +51.1 ‰. Four samples recovered from an old family in Kanazawa City (th46 through 50; Fig. 3b, shown by an enclosed circle with dot) and one from Tsushima (th65) were located along mixing line 2 that implies the saltpetre consists of Japanese domestic mixed with the British Indian origin. High $\delta^{15}\text{N}$ values of the th65 sample can be reasonably understandable, since large amounts of the pure saltpetre of British Indian origin were kept in the same clan, Tsushima, Nagasaki (Mizota et al., 2015).

Saltpetre samples, th46 throughout 50 were acquired from the Toh-hoh Family in Kanazawa City, Ishikawa Prefecture. The approximate ages of the gunpowder preparation are estimated to be around the late 1860's (Itagaki, 2010; Mizota and Yamanaka, 2014). The source saltpetre produced in Kanazawa City is known as an exclusive monopoly commodity, as made in the Gokayama Village (Itagaki, 2002) (Fig. 1; southern Toyama). Clear shift of $\delta^{18}\text{O}$ - $\delta^{15}\text{N}$ values of Japanese domestic saltpetre 1 (Fig. 3a; product of Gokayama) to the Kanazawa values (Fig. 3b; refer an enclosed circle with dotted line) along mixing line 2 is supported by old documents (Fig.

4; old document kept at The Archives of Modern History Records, Kanazawa City) in which purchase of large amounts (*c.* 4 metric tons) of saltpetre through Alt Co. located at Nagasaki was done at the end of October, 1867.

There can be seen surprising values, locating along mixing line 1 in Fig. 3b. The samples involve eight saltpetre samples in gunpowder which is applicable to the Japanese Tanegashima matchlock and/or early model of the Enfield rifle (sample ID: th38, th39, th40, th41 and th55 throughout th58 in Table 1a), all collected from Shohnai (present-day Yamagata prefecture) and Aki (present-day Hiroshima prefecture) clans. The oxygen and nitrogen isotopic values of four nitrate samples located at upper, left side (th38, th39, th56 and th57) are nearly identical with those for the Atacama Desert in South America (Fig. 3a) (Böhlke et al., 1997). Other two (th40 and th41) from Tsuruoka (Fig. 1) and two samples (th55 and th58) from Miyoshi (Fig. 1) located on the right, lower point on and around mixing line 1. The Japanese islands are located in humid climates where intensive leaching by meteoric precipitation prevails throughout the country. Therefore, the unique saltpetre with the desert isotopic signature is unlikely of local atmospheric deposition (Böhlke et al., 1997), but imported in form of saltpetre or gunpowder.

Such unique presence and its marketing route of this type of saltpetre would be recorded on the local historic documents. Extensive reference survey on the local publications revealed that the direct information relevant to the marketing route of the unique gunpowder exists. Details are given as follows. Shohnai clan had chances to contact with Prussian officials (Hakoishi, 2013), since there was given the appointment by Shogunate for task of patrolling the Edo-futyu since 1863. There exist several documents involving the endorsement and receipts, confirming that the clan purchased huge amounts of saltpetre, gunpowder, Pritchett patron, lead together with advanced type of rifles etc. by the Prussian weapon dealers, i.e., Conrad Gaertner and Frederik Hendrik Edward Schnell on 17 September, 1865, and March and July, 1868 (Sakata-shi, 1971), the dates preceding the initiation of Boshin War on 3rd January, 1868 and following the duration of the war. Two gunpowder samples (th38 and th39) studied in the present study had been kept by ancient families belonging to the Shohnai troop settled nearby a battle field in Kiyokawa where the first Boshin War happened on 24 April, 1868. $\delta^{18}\text{O}$ - $\delta^{15}\text{N}$ values (Fig. 3b) of the gunpowder reinforce the historic consequence of the marketing route originated from Prussian factory.

There exist two official documents kept at the Nagasaki custom house (Fig. 5), in which importation of huge amounts of saltpetre (one hundred barrels = 4.54 metric tons) together with gunpowder (one hundred barrels = 4.54 metric tons) by Aki clan on 13 and 24 March, 1868 is involved. Four gunpowder samples (th55 throughout th58) recovered from the ancient family in Miyoshi City, northern part of Hiroshima Prefecture may correspond to the historic document.

[void]

Binary plotting of the oxygen and nitrogen isotopic composition for nitrates as classified by category 2 is shown in Fig. 3c. As a whole, it is noticeable that the observed trend is similar to that of Fig. 3b, but higher frequency of the saltpetre with exotic origin. The $\delta^{15}\text{N}_{\text{nitrate}}$ values ranged from +0.4 to +26.4 ‰, where the concomitant $\delta^{18}\text{O}_{\text{nitrate}}$ showed more variable ranges from +2.2 to +54.1 ‰. The values for samples recovered from all paper cartridges applicable to most Enfield rifles (th74, th75, th78, th98, th99, 101 and th102), Sharps and Manceaur rifles located within a narrow range from +10.4 to +14.1‰ in $\delta^{15}\text{N}$ and +4.9 to +8.4 ‰ in $\delta^{18}\text{O}$ values. The overall isotopic trend is nearly consistent with that of nitrate from of British Indian origin (Fig. 3a). Such homogeneous isotopic values indicate large-sized manufacture as done in the Royal Gunpowder Mills of Waltham Abbey, located in the north of London, The United Kingdom. The corresponding figures for three samples applicable to the Enfield rifle (th94, th100 and th103 recovered from Kumamoto Prefecture) showed somewhat lower $\delta^{15}\text{N}$ and concomitant $\delta^{18}\text{O}$ values in ranges from +7.8 to 9.8 ‰ and +2.2 to 5.3‰, lying on mixing line 1. Five samples recovered from the copper-cartridge applicable to the Spenser rifle (th79, th83, th84, th90 and th91) showed more complicated values ranging from +3.7 to +15.5 and +5.8 to +37.7 ‰ in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values.

As similarly observed in Fig. 3b, ten samples located along or nearby mixing line 1 (Fig. 3c). The gunpowder applicable to the Lefauchaux (th81, th82, th92 and th93) and early model of the Smith & Wesson revolver (th85) represents the dominating Atacama Desert nitrate (th81, th82, th83, th92 and th93) mixed with the British Indian origin to lesser component (th91).

Three samples (th69, th70 and th71) located on the middle point on mixing line 1, all recovered from the Smith & Wesson 0.32 revolver. The plausible date of the assembly of the bullets is estimated around 1879, as revealed the records of the packing materials, which consist of Japanese traditional papers. The observed data may indicate temporal changes in source saltpetre from early (th85) to advanced models (th69, th70 and th71).

$\delta^{18}\text{O}$ - $\delta^{15}\text{N}$ value for th80 sample (recovered from pinfire cartridge applicable to Lefauchaux revolver) showed an anomalous value. Reasonable interpretation of the origin of nitrate is not given.

Two samples (th92 and th95) recovered from the cannon located denitrification trend. The cannon bullets were ejected, but not fired on the battle fields in Tabaruzaka (Ueki, Kumamoto, central Kyushu) in March, 1877. During the long-time burial conditions under moist soils for about hundred years, denitrification might be happened.

3.3. Implications for the discovery of the Atacama Desert nitrate in historic gunpowder

Previous studies (Mizota and Yamanaka, 2014; 2015, Mizota et al., 2014, 2015) on the

genetic origin of the saltpetre recovered from a diverse range of guns and cannon prevailing during the middle to late 19th century were argued on the basis of a single nitrogen isotopic composition. In the present study, a dual isotope technique was applied to improve our understanding of the origin. In addition to the Japanese domestic supplies mixed with those of British Indian origins. Atacama Desert nitrate derived from the atmospheric deposits was found in the saltpetre applicable to diverse types of matchlock guns, revolvers and rifles.

Sodium, magnesium and calcium nitrates make poor gunpowder because they are deliquescent. Valid gunpowder must stay dry. A prerequisite for the use of the desert nitrate in common explosives is that it must be converted into potassium nitrate by dissolving it in hot water and adding excess potassium salts. In early stages of the industrial processing, potash (wood ash), Russian potassium carbonate and kelp were used (Nishimura and Taguchi, 2000). On cooling potassium nitrate crystallizes out according to the following reaction:

The reaction is effective because the solubility of potassium nitrate decreases rapidly on cooling whereas the solubility of sodium chloride hardly decreases (Barnum, 2003).

There exist several limitations to access the archives (real documents), which are essential to trace historic events. In the middle to late 19th century, it has been well recognized that the Atacama Desert nitrate in South America, served as largest economic deposits in the world resource market (Wisniak and Garces, 2001; Saavedra, 2015). The large-scale exploitation did not begin until 1830 when shipments of the ore to Europe and USA began, mainly for nitrogen fertilizer rather than munitions. Nitrate mining in Tarapaca district (Chile) was greatly intensified since 1830's. Since the initiation of the export, the average annual export amounted to 63,000 metric tons. Subsequent rapid increase in the export of sodium nitrate associated with the Crimean war occurred from 1853 to 1856. Production and subsequent export of the sodium nitrate continuously increased up to 1912 when the large-scale commercial production of ammonia via Haber, followed by oxidation to nitric acid by the Ostwald processes, had been initiated in 1912 in Germany just before the outbreak of the World War I. During the 30 years of 1880 to 1913, the annual export increased 220,000 to 2,770,000 metric tons. Sum of the total production of the nitrate ore amounted 17,000,000 metric tons, of which 82 % was exported to Europe (Germany, 35 %; France, 17 %; Belgium, 11 %; The United Kingdom, 9 % and The Netherlands, 7 %) and the United States (16 %). Of total amounts of the imported nitrate, The United Kingdom consumed 82 %, Germany, France and The Netherlands, each 73 % for nitrogen fertilizer in agricultural sector, whereas the rests were consumed for chemical industries, as involving the conversion into saltpetre for explosives (Nishimura and Taguchi, 2000).

Under such circumstances, extensive potassium deposits consisting of carnallite (potassium ore) at Stassfurt mines near Magdeburg in northern Germany were exploited in 1861 (Rice and Davis, 1927), the date corresponding to the first industrial production of the conversion saltpetre in the world. Nitrate clipper continued to carry the Atacama Desert sodium nitrate into Germany to produce potassium nitrate for explosives until 1914 (Guttmann, 1895; Whittaker and Lundstrom, 1934; Takahashi, 2004; Travis, 2014). In the United Kingdom, Gatebeck Works was built in 1851. The Works had the earliest plant in England for manufacturing saltpetre from sodium nitrate. In the 1860s, the Wakefield Company pioneered a simple method for converting sodium nitrate into potassium nitrate. The following year of 1864, the Gatebeck Low Gunpowder Works in Cumbria (Great Britain) started a plant to manufacture potassium nitrate by essentially the same process. This is nowadays called the “Wakefield process”, after the owners of the company. Nevertheless, definite information on the source potassium for saltpetre production in the United Kingdom is not found.

Detailed description on the chemical process of the specific method for conversion of sodium nitrate into potassium nitrate in the industrial scale is not known in German and even English literatures. Instead, Tanba and Tawara (1895) gave the concrete description on the plants prevailed in Prussia in 19th century. The process involves two procedures, i.e., Chilean niter is reacted with potassium chloride (Anton’s procedure) or potassium carbonate (Nöller’s and Landmann-Schnitzer’s procedures). Highly purified saltpetre was recovered by subsequent, differential crystallization process. Although they did not refer any primary literatures in the article, there had probably been existed the common knowledge among the chemists in Prussia, since they made great efforts with self-study in the Prussian Empire for two (YT: 1890 to 1892) to three (KT: 1884 to 1887) years before development of the industrial fixation of atmospheric dinitrogen and subsequent conversion into nitrates. They also noticed that the annual import of Chilean niter into Hamburg harbor amounts 20,000, 72,700 and 305,500 tons in 1870, 1871 and 1889.

In the United States of America, DuPont Company played a major gunpowder industry in the frontier period, and provided *c.* 40 % of its demand for the Union during the Civil War. There are no documents that record to the conversion of South American sodium nitrate to potassium nitrate by DuPont Company (personal information from Lucas R. Clawson; Reference Archivist, Manuscripts and Archives Department, Hagley Museum and Library, Wilmington, Delaware, USA, provided on 10 Oct., 2015).

[void]

Gunpowder from four (th81, th82, th92 and th93) out of five specimens of Lefauchaux and one (th85) from early model of Smith & Wesson revolvers contains predominant saltpetre chemically transformed from Atacama Desert nitrate (Table 1c; Fig. 3a). Among them, three

copper-made cartridges (th82, th92 and th93) are keeping the head-stamp of Ely Brother's (London, UK) (Mizota and Yamanaka, 2014) that indicate manufacturing in the United Kingdom. According to the previous review of the United State of America (Van Gelder and Schlatter, 1927) and the United Kingdom (Croker, G, 1986), direct information relevant to the plausible location of the production brand, size and marketing route for other gunpowder (recovered from powder reservoirs: th38, th39, th55, th56, th57), and cartridges (metallic bullets: th69, th70, th71, th83) is not given.

Since the 1930's, similar potassium mining was initiated extensively in European countries. Being consistent with this historical evidence related to the world-wide saltpetre marketing, saltpetre with a unique isotopic signature was manufactured, as discovered in the several gunpowder applicable to muzzle (discovered in Kiyokawa Village, Yamagata Prefecture; Miyoshi City, Hiroshima Prefecture) and breech-loading types guns (Lefauchaux, Smith & Wesson revolvers and Spenser rifle), as a fossil of the industrial conversion involving sodium nitrate into potassium nitrate in the middle to late 19th century.

Both agricultural and explosive uses of the Atacama Desert nitrate were expendable, being hardly reserved under common human habitats. Present dual isotopic analysis provides direct evidence for the unique historic saltpetre intrinsic to the Atacama Desert nitrate as one of the predominating ingredients of gunpowder.

3.4. Historic prevalence of the pinfire cartridges applicable to Lefauchaux revolver

For better understanding the industrial conversion of the Atacama Desert nitrate into saltpetre, knowledge on the historic development of the pinfire cartridge is also significant, since the cartridges often involves unique saltpetre converted from the Atacama Desert nitrate. A pinfire cartridge as commonly applicable to Lefauchaux revolvers is an obsolete type of metallic firearm cartridge. The revolver was manufactured from the mid 1850's until the 1890's. Pinfire cartridges were supremely convenient in that they could contain percussion cap, gunpowder and projectile. They were available in a large number of caliber sizes for various types of weapons.

While pinfire shotguns declined from the early 1860's after introduction of mass-produced centerfire shotgun cartridges as like earlier models of Smith & Wesson revolver, the revolvers in particular became very successful and wide spread, being adopted by the armies of France, Italy, Spain, Switzerland and others. They were also used during the American Civil War (1861-1865). During the 1866 to 1872, Government of the United States of America released residual explosives, which were excess after the Civil War. Some of them were exported to Japan when the political regime was close to transforming from Tokugawas shogunate, resulting in the Boshin Civil War (1868 to 1869). Import of huge numbers of explosives including rifle,

saltpetre, gunpowder, percussion cup was recorded in the official custom documents in Nagasaki harbor, southwestern Kyushu, Japan (Mizota et al., 2015). Nevertheless, there is no records of importing the pinfire cartridges applicable to any types of revolver during the 1867 to 1872 (Mizota and Furukawa, unpublished).

In addition, commodity labels attached on the cartridge boxes would provide the direct information on the assembly. For purpose of easy handling and portability, the bullets applicable to Lefauchaux revolvers were packed in a paper or metallic box in each 25 to 50 units. Several boxes had been kept under well reserved conditions, and subject of private collections. Table 2 and Fig. 6a, b, c, and d summarize the lot of pinfire cartridge boxes (all applicable to Lefauchaux revolver) available on the internet. The results show wide-spread manufacturing of the bullets, particularly in western, central and southern Europe and the United States of America during the middle to late 19th century when the revolver prevailed. No box made in Japan is known.

4. Conclusion

British Indian vs. Japanese domestic origins of the saltpetre in historic gunpowder, which prevailed during the middle to late 19th century in Japan, had previously been argued based on the basis of single nitrogen isotopic analysis. Present study extends the previous analysis to apply the dual isotope technic involving the oxygen and nitrogen isotopic compositions, which provides direct evidence for tracking the origin. In addition to British Indian and Japanese domestic origins, nitrate from Atacama Desert formed by non-mass-dependent fractionation (reaction of NO_x with ozone) was discovered. Such unique saltpetre composes an ingredient of gunpowder applicable to diverse types of hand-guns. Historic consequence of the use of desert nitrate in manufacturing gunpowder was discussed on the basis of socio-economic documents.

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Figure caption

Fig. 1. A map showing the approximate location of the gunpowder and pure saltpetre samples analyzed in the present study. Only specific locations, which were discussed in the text are indicated.

Fig. 2. A photo showing the specimen of German (Prussian) saltpetre kept at the National Museum of Nature and Science, Ueno, Tokyo (Japan). A brown-colored label located at the lower, right-corner indicates saltpetre (written in *Kanji* letter) from Mayen, Rheinland, Germany (written in *Katakana* letter). (Photo: by courtesy of K. Momma)

Fig. 3. Binary plotting for oxygen and nitrogen isotope composition of nitrate from, (a); three end-member nitrates, (b); category 1 gunpowder and (c); category 2 gunpowder. For details, refer to the text. Explanations for mixing lines 1 and 2 and numerical letters associated with data points are given in the section of 3.2. Isotopic data for Atacama Desert nitrate are from Böhlke et al. (1997).

Fig. 4. Photographs showing the cover page of an account note, Nagasaki shop of Kanazawa clan (1867) (left). Documents in three lines from the right margin, written from top to down direction in classic Japanese that record the purchase of 66 bales (approximately 4 metric tons) of saltpetre from an English merchant Alt Co. at the end of October, 1867 (right).

Fig. 5. (a): A photo showing the cover page of the file of custom document (Document number: B 16 50-2) kept at the Nagasaki Museum of History and Culture at Nagasaki. The surface letters written by free-hand Japanese (in vertical direction) indicate that the document starts from the first January, 1868. (b): A page of the certificate for the purchase of hundred barrels of gunpowder on 13 March, and (c): hundred barrels of saltpetre, both through an English merchant, Rainbow, Lewis & Co. to Aki clan. (Photos: by courtesy of Y. Furukawa)

Fig. 6. Photographs showing the diverse cartridge boxes of the bullets applicable to Lefauchaux revolvers. Four examples are shown. (a): made in Germany, (b): made in the United Kingdom, (c): made in France and (d): made in the United States of America.

Source: <http://freemycollection.com/page=pinfire-cartridge-boxes>.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

a)

b)

c)

d)

Table 1a. Analytical data for category 1 gunpowder samples

Sample location ¹⁾	Type of guns ²⁾	Nitrate-N (%) ³⁾	Nitrate		
			Sample ID	$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)
Kiyokawa (Yamagata)	JTM	10.1	th38	-0.3	+44.8
Kiyokawa (Yamagata)	JTM	10.0	th39	+0.6	+41.2
Tsuruoka (Yamagata)	JTM	7.6	th40	+7.4	+21.4
Tsuruoka (Yamagata)	JTM	10.9	th41	+9.8	+15.6
Yonezawa (Yamagata)	JTM	11.1	th42	+7.6	+3.8
Yonezawa (Yamagata)	JTM	10.8	th43	+6.7	+4.6
Kanazawa (Ishikawa)	Enfield rifle	10.3	th44	+8.7	+5.0
Kanazawa (Ishikawa)	Enfield rifle	11.2	th45	+8.8	+4.3
Kanazawa (Ishikawa)	Enfield rifle	8.5	th46	+10.5	+4.5
Kanazawa (Ishikawa)	Enfield rifle	10.8	th47	+9.9	+5.0
Kanazawa (Ishikawa)	Enfield rifle	7.8	th48	+10.0	+6.6
Kanazawa (Ishikawa)	Enfield rifle	12.4	th49	+10.1	+5.5
Kanazawa (Ishikawa)	Enfield rifle	13.1	th50	+10.5	+5.1
Kanazawa (Ishikawa)	Enfield rifle	13.8	th51	+9.0	+3.9
Kochi (Kochi)	JTM	12.5	th52	+5.7	+3.8
Kochi (Kochi)	JTM	12.1	th53	+5.5	+4.7
Kochi (Kochi)	JTM	10.0	th54	+5.5	+3.4
Miyoshi (Hiroshima)	JTM	11.8	th56	+0.3	+51.1
Miyoshi (Hiroshima)	JTM	11.1	th57	+1.0	+43.6
Miyoshi (Hiroshima)	JTM	11.0	th55	+5.9	+30.7
Miyoshi (Hiroshima)	JTM	11.3	th58	+9.6	+19.7
Tsuwano (Shimane)	Enfield rifle	9.8	th59	+5.9	+3.7
Tsuwano (Shimane)	Enfield rifle	11.0	th60	+6.8	+3.1
Tsuwano (Shimane)	Enfield rifle	11.2	th61	+6.4	+4.0
Tsuwano (Shimane)	Enfield rifle	11.7	th62	+6.4	+4.9
Tsushima (Nagasaki)	JTM	10.1	th63	+7.4	+2.9
Tsushima (Nagasaki)	JTM	13.0	th64	+7.3	+3.5
Tsushima (Nagasaki)	JTM	10.5	th65	+11.7	+5.4
Saga (Saga)	Primer for cann	12.7	th66	+7.0	+4.2
Idzumi (Kagoshima)	JTM	10.6	th67	+8.5	+3.8
Idzumi (Kagoshima)	JTM	9.0	th68	+9.1	+4.6

1) Location is arranged in a decreasing order of the Northern Hemisphere latitude

2) JTM = Japanese Tanegashima matchlock

3) Refer Mizota and Yamanaka (2014, 2015), Mizota et al., 2014

Table 1b. Analytical data for category 2 gunpowder samples

Sample location ¹⁾	Type of guns	Nitrate-N (%) ²⁾	Sample ID	Nitrate	
				$\delta^{15}\text{N}$ (‰)	$\delta^{18}\text{O}$ (‰)
Hagi (Yamaguchi)	Smith & Wesson .32 revolver	13.8	th69	+5.4	+33.1
Hagi (Yamaguchi)	Smith & Wesson .32 revolver	12.4	th70	+7.5	+25.5
Hagi (Yamaguchi)	Smith & Wesson .32 revolver	11.5	th71	+6.4	+29.7
Takeo (Saga)	Enfield rifle	12.2	th74	+13.5	+5.1
Takeo (Saga)	Enfield rifle	12.0	th75	+14.1	+5.5
Takeo (Saga)	Sharps rifle	12.7	th76	+12.6	+8.4
Takeo (Saga)	Sharps rifle	12.6	th77	+13.6	+6.8
Gyokutoh (Kumamoto)	Enfield rifle	10.5	th78	+12.2	+5.9
Gyokutoh (Kumamoto)	Spenser rifle	10.5	th79	+12.9	+6.1
Gyokutoh (Kumamoto)	Spenser rifle	11.5	th83	+3.7	+37.7
Gyokutoh (Kumamoto)	Spenser rifle	11.3	th84	+13.5	+5.8
Gyokutoh (Kumamoto)	Manchau rifle	11.7	th86	+13.5	+4.9
Gyokutoh (Kumamoto)	Manchau rifle	11.0	th87	+12.9	+5.7
Gyokutoh (Kumamoto)	Lefauchaux revolver	11.2	th80	+5.7	+15.6
Gyokutoh (Kumamoto)	Lefauchaux revolver	11.2	th81	+0.9	+48.1
Gyokutoh (Kumamoto)	Lefauchaux revolver	12.1	th82	+1.6	+54.1
Gyokutoh (Kumamoto)	Smith & Wesson .32 revolver	11.9	th85	+2.1	+45.0
Ueki (Kumamoto)	Enfield rifle	9.1	th94	+9.8	+2.2
Ueki (Kumamoto)	Spenser rifle	9.4	th90	+13.1	+6.3
Ueki (Kumamoto)	Spenser rifle	8.2	th91	+10.9	+12.7
Ueki (Kumamoto)	Manchau rifle	9.5	th88	+12.9	+6.2
Ueki (Kumamoto)	Manchau rifle	9.9	th89	+13.2	+5.9
Ueki (Kumamoto)	Lefauchaux revolver	10.6	th92	+4.0	+45.6
Ueki (Kumamoto)	Lefauchaux revolver	6.8	th93	+0.4	+48.9
Tabaruzaka (Kumamoto)	Cannon	5.9	th95	+19.0	+11.0
Tabaruzaka (Kumamoto)	Cannon	5.5	th96	+13.6	+6.8
Tabaruzaka (Kumamoto)	Cannon	1.0	th97	+26.4	+17.0
Kumamoto (Kumamoto)	Enfield rifle	10.8	th98	+13.7	+7.5
Kumamoto (Kumamoto)	Enfield rifle	11.0	th99	+13.2	+7.4
Kumamoto (Kumamoto)	Enfield rifle	10.7	th100	+7.8	+4.8
Kumamoto (Kumamoto)	Enfield rifle	10.7	th101	+10.4	+5.8
Kumamoto (Kumamoto)	Enfield rifle	10.7	th102	+12.0	+5.4
Kumamoto (Kumamoto)	Enfield rifle	11.1	th103	+8.4	+5.3

1) Location is arranged in a decreasing order of the Northern Hemisphere latitude

2) Refer Mizota and Yamanaka (2014), Mizota et al. (2014)

Table 1c. Analytical data for Prussian saltpetre, nitratine ore and commercial NaNO₃ fertilizer specimens kept at Japanese institutions

Sample	Location	Sample ID	Acquisition		Water-soluble		Nitrate	
			Institution	Date	K (%)	N _{nitrate} (%)	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)
Prussian saltpetre ¹⁾	Mayen, Rheinland, Prussia	th144	National Museum of Nature and Science, Tokyo (NSM-MF 00703)	C. 1877~1916	42.5	13.2	+2.4	+42.8
Rough nitratine ore	Traoaca, Atacama Desert, Chile	th145	<i>Ditto</i> (NSM-MF 11006)	Early 1940's	-	2.9	+1.2	+52.0
		th146	<i>Ditto</i> (NSM-MF 11006)		-	3.6	+0.6	+52.7
		th147	<i>Ditto</i> (NSM-MF 11006)		-	9.5	+1.2	+54.2
Commercial NaNO ₃ fertilizer ²⁾	Tsukuba, Ibaraki, Japan	th143	National Institute for Agro-Environmental Sciences	C. 1930's	-	-	+0.5	+52.8
		th142	<i>Ditto</i>	1990's	-	-	+0.7	+52.9
		th118	Market in Sapporo, Hokkaido ³⁾	2003	-	-	+0.5	+53.8
		th119	<i>Ditto</i>	2015	-	-	-0.2	+54.7

1) Refer Fig. 2

2) Imported from Atacama Desert (Chile) and highly purified

3) Exclusively applied for sugar beet cultivation in Hokkaido, northern Japan

-: Not determined

Table 2. Lot of pinfire cartridge boxes applicable to Lefauchaux revolver as shown by country

Caliber (mm)	Number of lot						
	Germany	United Kingdom	France	USA	Czechoslovakia	Italy	Belgium
5	5	3	3	0	0	2	0
7	11	5	6	3	3	0	0
9	10	1	2	3	1	0	1
12	5	0	5	4	0	0	1
15	0	0	2	0	0	2	2

Data source URL: [http://freemycollection.com/page=pifire-cartridge boxes](http://freemycollection.com/page=pifire-cartridge+boxes)