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Stable isotopic characterization of gunpowder ingredients from the mid to late nineteenth century in Japan

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A B S T R A C T

During the gunpowder-driven military revolution in early modern Japan, a huge amount of ammunition and its ingredients was imported from western countries and manufactured locally. A sum total of 24 gunpowder ingredients which survived from during the time was analyzed for $\delta^{15}N_{\text{saltpetre-nitrogen}}$, $\delta^{34}S_{\text{native sulfur}}$ and $\delta^{13}C_{\text{charcoal carbon}}$. $\delta^{13}C_{\text{charcoal carbon}}$, and these analyses revealed values in a narrow range from −27.6 to −25.7‰, indicating a C_3 dominant wood carbon source. In contrast, $\delta^{34}S_{\text{native sulfur}}$ showed fairly large variation (−1.1 to +12.3‰), and this variation reflects distinct source sulfur. High $\delta^{34}S_{\text{native sulfur}}$ values (around +10‰) correspond to Sicilian sulfur (Italy) which prevailed in the world sulfur market at the time. Low $\delta^{34}S_{\text{native sulfur}}$ values (∼−1.1‰) were observed for a few gunpowders (Enfield rifle, Le Faucheux revolver and artillery guns), implying a predominance of Japanese volcanic sulfur.

$\delta^{15}N$ values of nitrate-nitrogen in the form of saltpetre also varied from −2.0 to +22.0‰. Such variation was interpreted in terms of contributing two end-member nitrates, i.e., nitrate formed by a nitrification process (microbial origin), and nitrate from desert nitrate (meteoric origin: around 0‰). An anomalously high $\delta^{15}N$ value (+22.0‰) observed for a cannon type artillery was likely a residue that was subjected to denitrification during burial in soils. Information from stable isotope analysis for saltpetre and native sulfur, but not from charcoal carbon, provides strong evidence for the provenance reflecting worldwide trading lead by some advanced nations.

1. Introduction

Abrupt change in the political system of human society often requires great military force. Regime change during the mid to later nineteenth century in Japan was characterized by two civil wars, or ‘gunpowder-driven military revolutions’. The Boshin-war began in January 1868 and continued until May 1869, followed by the Seinan-war in 1877. The propellant used by military forces in the wars was gunpowder, which is a solid mixture of saltpetre (KNO_3), native sulfur and charcoal carbon in an approximate proportion of 75:15:10 (Gray et al., 1982). Demand for supply and use of the ammunition reached its zenith during this period. Numerous socioeconomic, historical and technical studies have been conducted in relation to the production and distribution of gunpowder in Western Europe (e. g., Buchanan, 2006; Frey, 2009; Cressy, 2011) and Japan (Itagaki, 2002a,b). Nevertheless, there has been very limited geochemical characterization of each ingredient, probably due to lack of well preserved specimens.

Light-element stable isotope geochemistry can narrow the plausible origins of each ingredient. $\delta^{15}N$, $\delta^{34}S$ and $\delta^{13}C$ values are useful tracers for saltpetre, native sulfur and charcoal carbon, respectively. Table 1 summaries existing documentation relevant to the starting materials for gunpowder manufacture during the period of exchange between United Kingdom and Japan. Here, we emphasize that there exists no stable isotope measurement of saltpetre-nitrogen.

Recently we had an opportunity to analyze the well preserved specimens of saltpetre and gunpowder ingredients which prevailed during the mid to late nineteenth century. In the present study, chemical and stable isotopic results are discussed in the context of historical documents relevant to the origins of the gunpowder ingredients.

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2. Materials and methods

2.1. Brief description of sample materials

Samples analyzed in the present study are summarized in Table 2 with a brief description of each. In the table, samples are arranged from nitrous-earth (top row) starting material for saltpetre manufacture, and crude saltpetre product, to three types of gunpowder ingredients (bottom).

A nitrous-earth from northern Thailand was taken in August 2010 from an abandoned lead mine cave floor that is currently forming by deposition of fruit-bat guano under tropical weather conditions. According to oral information from local inhabitants, the deposit has been used for source material for local saltpetre production up to recent times, although no written scientific documentation exists. The sample represents a typical source material for prompt saltpetre manufacture under tropical condition as in British India as discussed later.

Five crude saltpetre specimens were selected from the comprehensive collections of four local ethnic museums located at Gokayama, southernmost Toyama. This area has been preserved as a UNESCO World Heritage site, retaining unique housing systems in a mountain village adapted for heavy snow. Production of saltpetre in the area started in the late sixteenth century and continued up to the early Meiji era. Details of the biochemical and technical processes related to saltpetre manufacture are given by Itagaki (2002a,b; 2010). The principle is nearly the same as done in European countries (Williams, 1975; Barnum, 2003). Brief account has been given in the latter part of Section 3.2. The saltpetre manufacture was a monopoly of the Kaga clan, and many tools and relevant documents are kept under well preserved conditions. The sample materials represent crude saltpetre manufactured by bioengineering in the late nineteenth century in Japan.

Gunpowder samples for use in hand held weapons to large artillery pieces were collected throughout Japan (Table 2). The gunpowder samples were classified into three groups on the basis of the type. Gunpowder type 1 represents four (from Kiyokawaguchi museum and The Doho's) and two (for Enfield rifle: muzzle loader type gun) intact gunpowder samples acquired from local museums and personal collections. These ingredients were fully packed in Japanese traditional papers. A production date of 1843 was marked on the paper package of the Kiyokawaguchi specimens. The gunpowder would have been used for the Japanese Tanegashima matchlock gun which represents a muzzle loader type hand gun that prevailed in the Shonai clan. For the Doho's specimens, detailed chemical analysis together with the relevant historical significance have been given by Itagaki (2010). Plausible source materials for the saltpetre, native sulfur and charcoal carbon suggest the ingredients consist of saltpetre manufacture in Gokayama village, sublimated sulfur from an active fumarole in Tateyama volcano and shrub marijuana (*Cannabis sativa*) from the Noto area, all local sources within Kaga clan territory. The gunpowder was probably prepared at the Tuchyozu gunpowder factory located in southern Kanazawa around 1872. Firing tests showed that the gunpowder is highly explosive (Itagaki, 2010). Gunpowder type 1 was reportedly prepared in Japan.

Gunpowder type 2 represents 15 ingredient samples extracted from metal (Spencer rifle, Le Faucheux revolver and Smith and Messon 32 revolver) and paper (Manceau rifle) cartridges for breech loader type hand guns. It has been reported that the cartridges were imported from western countries during the mid to late nineteenth century and kept intact by ancient families.

Gunpowder type 3 represents three gunpowder samples recovered from bombs for artillery guns used during the Seinan-war in mid to late March, 1877 at Tabaruzaka, Kumamoto (present-day, Ueki and Gyokutoh towns). The bombs were certainly unexploded and in nearly intact conditions of ingredients for Armstrong cannon and Mountain gun used with a 4 Kg cannonball. An upper part of the sphere-form bomb (cannon) is transformed by physical force and there could be seen marked iron rust inside the sphere. They were probably recovered from the soil after a certain period of burial. Partial leaching loss of some ingredients by penetrating groundwater, particularly highly water-soluble saltpetre, is plausible, and secondary deterioration may have happened as a result.

2.2. Analytical methods

Before applying the mass spectrometric analysis for each gunpowder ingredient, pretreatment is required. Saltpetre is highly soluble in water, whereas the other associated constituents native sulfur and charcoal carbon have limited solubility. Saltpetre can be separated by a selective chemical dissolution technique involving extraction with water. From 50 (for crude saltpetre and gunpowder samples) to 1000 mg (for a nitrous-earth sample) of air-dried powder was extracted by this technique. One drop of ethanol was added to the suspension to suppress water repellance and facilitate the dissolution. The extract was quantitatively separated using an ADVANTEC membrane filter with the pore size of 0.45 μm under vacuum. The residues (native sulfur and charcoal carbon) on the

Table 1
Summary of literature review: source materials for gunpowder manufacture in United Kingdom and Japan during the mid to later nineteenth century.

Country	Ingredient of gunpowder	Reference	
		Prompt location of source materials	Expected stable isotopic ratios
United Kingdom	Saltpetre	Grough saltpetre from Bihar and Bengal, British India[a]	$\delta^{15}N$ = variable, depending on microbial or meteoric in origin
	Native sulfur	Brimstone from Sicily, Italy[b]	$\delta^{34}S = +10$‰ (an average value)[c]
	Charcoal	Plantation of alder, willow or dogwood grown at Waltham Abbey in Essex, UK[d]	$\delta^{13}C = -27$‰[e]
Kaga clan, Japan	Saltpetre	Crude saltpetre transported from Gokayama[f]	$\delta^{15}N$ = variable, depending on microbial process
	Native sulfur	Refined sulfur from Tateyama volcano[f]	$\delta^{34}S = +2$‰ (an average value)[g]
	Charcoal	Stem of marijuana from Noto[h]	$\delta^{13}C$ = heavier than -29‰[i]

[a] Gray et al. (1982); Hall (1997); Balasubramaniam and Kishan (2005); Buchanan (2006); Frey (2009); Cressy (2011).
[b] Goodenough (1868); Hunt (1915); Lundy (1959); Mormino (2004).
[c] Dessau et al. (1962).
[d] Gray et al. (1982).
[e] Codron et al. (2005).
[f] Itagaki (2002a,b, 2010).
[g] Ueda et al. (1979); Kusakabe et al. (1983).
[h] Itagaki (2010).
[i] West et al. (2009).