



Dual (oxygen and nitrogen) isotopic characterization of the museum archived nitrates from the United States of America, South Africa and Australia

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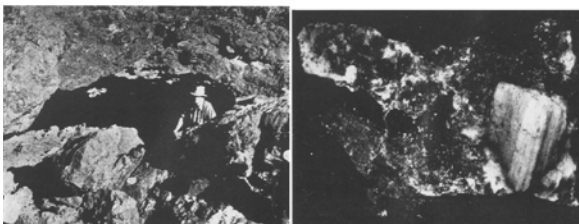
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HIGHLIGHTS

- Stable isotopic characterization of the museum archived nitrates was made.
- Most nitrates consist of K⁺-nitrates with less Na⁺-nitrates.
- $\delta^{15}\text{N}$ - $\delta^{18}\text{O}$ relationships of nitrates indicate microbial origin.
- Formation conditions of nitrate under extensive evaporative concentration were inferred.

GRAPHICAL ABSTRACT

Museum archived nitrate mineral (London, UK in 1930) is the revival legacy for stable isotope study



Entrance to the cave where nitrate deposit occurs

Close-up of euhedral potassium nitrate

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ABSTRACT

Dual (oxygen and nitrogen) isotopic composition of the museum archived nitrates from the United States of America, South Africa and Australia was studied. The analyzed specimens were collected in middle 19th to early 20th centuries, and represent world-wide acquisition of the Smithsonian Institution Natural Museum of Natural History (Washington, D. C., USA) and the Natural History Museum (London, UK). The samples consist of transparent to semi-transparent aggregates of minute nitrate, euhedral crystallites which imply precipitation from percolating fluids under ample space and dry regimes. The major nitrate chemistry is saltpetre (KNO₃) with minor nitratine (NaNO₃). A binary plot of $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of almost all nitrates indicates a trend, reflecting microbial origin through nitrification of ammonium. The diagram excludes the contribution of meteoric origin formed by mass-independent, photochemical reaction of NO with ozone in stratosphere. Calculated paleo-ambient fluid compositions responsible for microbial nitrification imply extreme evaporative concentration of relevant fluids under dry climatic regimes in the Northern Cape Province (South Africa) and in the Northern Territory (central Australia), and even throughout the United States of America. The dual isotopic characterization provides direct evidence to the origin of the museum archived nitrates.

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1. Introduction

Saltpetre (KNO_3) constitutes one of the major gunpowder ingredients which played a driving force on changes in world-wide political regimes during the 16th to 19th century (e. g., Buchanan, 2006; Sun, 2013; Güldner et al., 2016). The salt seldom occurs as an economic ore deposit in a natural state (Whittaker and Lundstrom, 1934; Hubbard Jr., 2012; Steiger, 2016). The mineral is far from the only compound in the cave sediment commonly referred to as saltpetre. The nitrate minerals contained therein are notoriously deliquescent, meaning that they absorb moisture from the air and eventually change into solution. Hence, nitrate compounds such as Na^+ , Mg^{2+} and Ca^{2+} -nitrates rarely crystallize into their naturally-occurring forms (nitratine, nitromagnesite and nitrocalcite, respectively) in humid environments with high relative humidity. Instead, during the late Medieval to early Modern times, human-induced saltpetre manufacture used classic biotechnology in which nitrous earths were used as original source materials (Mizota et al., 2016). Upon the urgently increased demands for saltpetre in times of war, harbor blockades stimulated reconnaissance for potential sources of natural occurring nitrates, particularly in the United States of America (Whisonant, 2001; Blankenship et al., 2009; O'Dell and George, 2014). The historic review of mining and partial chemical analysis of nitrate deposits from caves has been documented for selected sites in numerous government papers (Gale, 1912; Mansfield and Boardman, 1932; Whittaker and Lundstrom, 1934). Historic saltpetre for gunpowder manufacture can be generated by reaction of crude nitrates such as Na^+ , Ca^{2+} and Mg^{2+} with mined potassium ore, as likely prevailed in early to middle 19th century Prussia (Mizota et al., 2016).

There have been contradictory arguments to their site of origin of nitrates, as reviewed by Hill (1981a, 1981b). Some hypothesis involved derivation from animal waste followed by evaporative concentration from percolating groundwater. Heaton (1987) and Sandler and Heaton (1997) analyzed $\delta^{15}\text{N}$ values of several nitrate minerals from South Africa and Israel, respectively. Their interpretation relevant to the mode of formation is inconclusive due to lack of firm evidence. Full understanding on the process awaits further evidence directly related to the origin, as evidenced by the use of $\delta^{15}\text{N}$ in combination with $\delta^{18}\text{O}$ analysis (Böhlke et al., 1997; Kendall, 1998; Mizota et al., 2016). The objective of the present study is to characterize the museum archived nitrate minerals from the world-wide acquisitions of two institutions, the Smithsonian Institution Natural History of Museum (Washington, D. C., USA) and the Natural History Museum (London, UK). Such an interdisciplinary approach is rarely made for historic specimens.

2. Materials and methods

Natural caves, particularly limestone caves and rock shelters, often provide potential deposits of nitrate minerals where meteoric leaching after their formation is hindered. Nevertheless, previous so-called “saltpetre caves” are closed for conservation or have collapsed after mining activity. Instead, extensive reconnaissance of the existing world-wide database and subsequent call for sharing of samples was made for historic nitrate specimens in national and local institutions. As a consequence, we were given an opportunity to study unique specimens of nitrate minerals acquired before ca. 1920/1930 in the collection of the Smithsonian Institution National Museum of Natural History (Washington, DC; The United States of America) and the Natural History Museum (London; The United Kingdom). The studied sample specimens are summarized in Table 1.

2.1. Description of nitrate samples

2.1.1. Nitrates from the United States of America

When considering the political and economic conditions in the United States during the early 19th century, government oriented-

reconnaissance survey of the nitrate deposits for potential resources for gunpowder ingredients is certainly reasonable. From the early 19th century (1807) through the American Civil War (1861–1865), caves in Kentucky, Tennessee, Virginia, West Virginia, Alabama, Georgia, Arkansas, and Missouri were important source of nitrates, an essential ingredient of gunpowder. There are about 17,000 known caves in the United States. They occur in every State except for Rhode Island and Louisiana (Hill, 1981a, 1981b; Davies and Morgan, 1991). Upon the abruptly increased demand for saltpetre for the gunpowder industry, the cave nitrates served as a major potential source (DePaepe and Hill, 1981). Prior to this time, the United States and earlier American colonies had not developed an extensive saltpetre industry, and relied heavily on imported gunpowder and refined saltpetre from the United Kingdom. In regions of British India, high concentrations of potassium nitrate were naturally found in certain surface deposits, which gave the UK control over one of the world's most extensive and easily obtainable supplies of saltpetre (Buchanan, 2006). Imported UK saltpetre was of such high quality and low cost that U. S. domestic sources were often not worth mining, i.e., domestic saltpetre production and gunpowder production were not economically viable.

A list of saltpetre caves or rock-shelter whose dirt was removed for nitrate processing or production for saltpetre is documented (Plemons, 2006). It became widely known that nitrates were plentiful in many of the dry caves in the United States. Prospecting has occurred throughout the United States (Alabama, Arkansas, Georgia, Illinois, Indiana, Kentucky, Maryland, Minnesota, Missouri, North Carolina, Ohio, Pennsylvania, Tennessee, Texas, Virginia and West Virginia) (Plemons, 2006). Surface or near-surface evidence of nitrate salts have been examined from coatings on rock walls, fill cracks and crevices, and mixed with cave earth. Although no accurate records of production were kept, it has been estimated that over 15,000 tons of niter earth (producing 200 tons of potassium nitrate) were removed from Mammoth Cave in Kentucky between 1811 and 1814 (Davies and Morgan, 1991). Nevertheless, the origin of the nitrate salts is not clearly understood, but the salts are believed to result from the action of nitrifying bacteria (Hill, 1981a, 1981b) on organic nitrogen compounds.

A sum total of eleven nitrate specimens from the US were examined in the present study. The specimens include those from western (Oregon, Nevada and California) and mid (Arkansas) United States of America. A brief description of the nitrate deposits is given in several government publications from the Geological Survey and Ministry of Agriculture of the United States (Gale, 1912; Mansfield, 1915; Nobel and Mansfield et al., 1922; Mansfield and Boardman, 1932; Whittaker and Lundstrom, 1934). Detailed location of these nitrate samples is documented in the relevant references (Gale, 1912; Mansfield, 1915; Noble and Mansfield, 1922; Nobel, 1931; Plemons, 2006). For seven nitrate samples from Oregon State (La. ID; th127, 129, 130, 131, 132, 134 and 135), locality of each mine is indicated by classic datum (abbreviated notation) in the historic document (Mansfield, 1915). Due to lack of relevant inventory, the task is hardly difficult to convert into current, commonly prevailing geodetic datum system (longitude and latitude) in the world. There may be demands for comparison among these mines, when broader readers encounter to discuss the baseline information on the spatial variation in the analytical data, particularly stable isotopic signatures. Use of these abbreviated notations in the present study was avoided, because the direct citation of the abbreviated notations without conversion does not sound meaningful. Therefore, we have decided not to cite these specific notations. Instead, it was considered that some ones who want to know more detailed location could refer the literatures, as indicated in the right-end column in Table 1 and associated footnote. The final choice follows the writing styles common in diverse international journals of natural science.

A photo of niter from Searcy County, northern Arkansas is shown in Fig. 1a. The specimen consists of transparent to semi-transparent, euhedral aggregates of crystallite potassium nitrate (Fig. 1a).

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