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Alida Pérez-Fodich[1,2], Martin Reich[1,2]*, Fernanda Álvarez[1,2], Glen T. Snyder[3], Ronny Schoenberg[4], Gabriel Vargas[1,2], Yasuyuki Muramatsu[5], and Udo Fehn[6]
[1]Department of Geology, Universidad de Chile, Plaza Ercilla 803, Santiago, Chile
[2]Andean Geothermal Center of Excellence (CEGA), Universidad de Chile, Santiago, Chile
[3]Department of Earth Science, Rice University, Houston, Texas 77251-1892, USA
[4]Department of Geoscience, University of Tübingen, Wilhelmstrasse 56, D-72074, 72074 Tübingen, Germany
[5]Department of Chemistry, Gakushuin University, Tokyo 171-8588, Japan
[6]Department of Earth and Environmental Sciences, University of Rochester, Rochester, New York 14627, USA

ABSTRACT

The giant nitrate deposits of the hyperarid Atacama Desert (Chile) are one of the most extraordinary, yet enigmatic, mineral occurrences on Earth. These deposits are complex assemblages of highly soluble nitrates, chlorides, sulfates, perchlorates, iodates, and chromates, and their preservation is the result of prevalent hyperarid climate conditions in the Atacama Desert since the late Miocene, with average rainfall rates of <10 mm/yr in the past ~3 m.y. Although several hypotheses have been proposed since the mid-1800s, the formation of these extensive deposits still remains highly controversial despite the fact that recent studies have argued toward an atmospheric source for the nitrate, sulfate, and perchlorate components. In this report, we focus on the often overlooked and poorly studied iodine and chromium components of Atacama's nitrates. We present the first cosmogenic iodine (^{129}I) and stable chromium ($\delta^{53/52}$Cr) isotope data of nitrates showing that groundwater has played an unforeseen role in the formation of these massive deposits. The isotopic signature of I in the nitrates (^{129}I/I ~150–600 × 10^{-15}) share similarities with deep sedimentary (marine) pore waters and shales, deviating significantly from atmospheric iodine (^{129}I/I ~1500 × 10^{-15}), while the positive and highly fractionated $\delta^{53/52}$Cr$_{SRM979}$ values (+0.7‰ to +3‰) are indicative of intense Cr redox cycling due to groundwater transport. Our evidence points toward a multi-source genetic model for the Atacama Desert nitrate deposits, where these extensive accumulations were the result of long-lived, near-surface mineral precipitation driven by groundwater (i.e., chromates, iodates) coupled with dry atmospheric deposition (i.e., nitrates, perchlorates) and sea spray inputs (i.e., sulfates, chlorides), triggered by increasing aridity and tectonic uplift.

INTRODUCTION

Massive nitrate accumulations on Earth's surface are scarce and their existence is restricted to hyperarid environments like the Atacama Desert of northern Chile, although minor amounts of nitrate are present in other desert environments such as Death Valley (western United States), the Gobi Desert (Turpan-Hami area, northwestern China), and the McMurdo Dry Valleys (Antarctica) (Ericksen, 1981; Ericksen et al. 1988; Michalski et al., 2005; Qin et al., 2012). The Atacama deposits are unique in terms of their massive extent and diversity in chemical and mineralogical compositions. First, they are the largest nitrate accumulations in the world, making up an almost continuous ~700-km-long by ~20-km-wide belt (Fig. 1), and have been the premier source for natural nitrate since the 1800s. The nitrate deposits of Atacama are also singular due to the presence of unusual oxidized components such as iodates, chromates, and perchlorates, hosted by a complex mineral bed ~0.2–3 m thick composed of nitrates, sulfates, and chlorides. These unique features have puzzled geologists since Darwin's visit to Atacama in 1835, and several hypotheses have been proposed to explain their origin (Ericksen, 1981). Most recent studies have focused on the
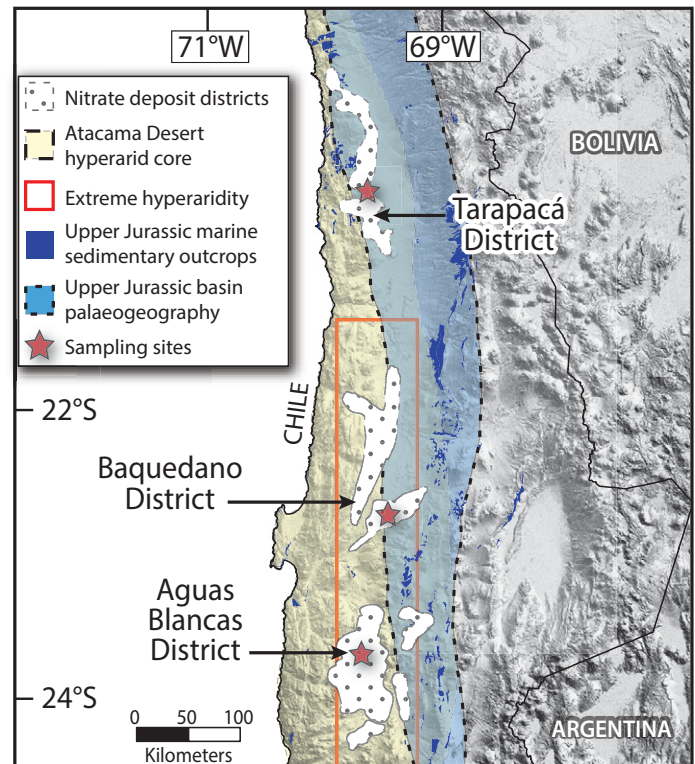

Figure 1. Map of Atacama's nitrate deposits displayed on digital elevation model of northern Chile. Location and distribution of nitrate deposits is shown in white dotted areas. Atacama Desert hyperarid core is shown in light yellow, and paleogeographic reconstruction of Jurassic Andean Basin (Vicente, 2006) is shown in light blue. Distribution of Upper Jurassic marine sedimentary outcrops (Mpodozis et al., 2005) is indicated in dark blue. Red rectangle shows extreme hyperarid area of Atacama Desert.

nitrogen, sulfur, and triple oxygen isotopic signatures from the abundant nitrate and sulfate mineral salts, and rare perchlorate compounds (Böhlke et al., 1997; Bao and Gu, 2004; Michalski et al., 2004). Oxygen, and to a lesser extent nitrogen, isotope data indicate that there is a significant atmospheric influence in nitrate formation related to dry deposition, while sulfur and oxygen data in sulfates indicate an influence of atmospheric, terrestrial, and marine sources (Böhlke et al., 1997; Rech et al., 2003; Michalski et al., 2004). Perchlorate, on the other hand, has a distinct atmospheric signature according to triple oxygen isotope values (Bao and Gu, 2004). Despite these recent advances, available geochemical and isotopic data on nitrate, sulfate, and perchlorate are not sufficiently diagnostic to yield a genetic model that explains the occurrence of all mineral components, including the exotic iodates and chromates. Iodine (I) occurrence

*E-mail: mreich@ing.uchile.cl

is so exceptional that Atacama's nitrates are currently the world's prime source for I, with concentrations in the range of hundreds to thousands of parts per million (ppm), ~3–4 orders of magnitude higher than the average I content of the continental crust. Chromium (Cr), on the other hand, is widespread in the Atacama nitrates in the range of tens of parts per million, but can also be sufficiently enriched as Cr(VI) to form chromate-bearing minerals. In this report, we propose a multi-source model for the genesis of the nitrate deposits of Atacama that (1) explains the presence of the exotic iodine and chromium components, (2) integrates their occurrence to the most common compounds, such as nitrate and sulfate, and (3) incorporates the previously unforeseen role of groundwater, constraining nitrate deposit formation to an outstanding convergence of tectonic, hydrologic, and climatic conditions that favored the long-lived fixation and accumulation of chemical components from the atmosphere and subsurface water.

SAMPLES AND METHODS

We used ^{129}I/I isotopic ratios measured in nitrate ores to determine the source of iodate as an expression of the deviation from the pre-anthropogenic meteoric/atmospheric value of 1500×10^{-15} [at·at^{-1}], typical of surficial reservoirs (meteoric water, seawater, and sea spray) uncontaminated with ^{129}I from nuclear weapons testing and fuel reprocessing (Fehn et al., 2007). In addition, stable isotopes of Cr ($\delta^{53/52}$Cr) were used to constrain the source of chromate in the nitrates, and to test the involvement of redox cycling between soluble Cr(VI) and insoluble Cr(III) in groundwater (Schoenberg et al., 2008).

To obtain ^{129}I/I ratios, 30–50 g of powdered nitrate samples were diluted in 100 mL of deionized water, to release iodine as IO_3^-. Iodine was extracted into carbon tetrachloride, then back-extracted by a Na-bisulfite solution and precipitated as ~2 mg AgI targets. Iodine isotopic ratios were measured using accelerator mass spectrometry at the PRIME Lab, Purdue University (Indiana, USA).

To determine the $\delta^{53/52}$Cr values of chromate components in nitrate, 100–300 mg of sample was dissolved in 1.2 mL of deionized water, and was centrifuged to remove the minor detrital fraction. A ^{50}Cr-^{54}Cr spike solution of known composition was added to the supernate. Cr purification followed the anion-exchange and liquid-liquid extraction methods established by Schoenberg et al. (2008). Cr isotope analyses were performed on a Neptune Plus multicollector–inductively coupled plasma–mass spectrometer (MC-ICP-MS) at the University of Tübingen (Germany). Cr isotope data are given in the δ notation relative to the chromium standard NIST SRM 979 (National Institute of Standards and Technology [NIST] standard reference material [SRM]).

RESULTS AND DISCUSSION

The ^{129}I/I ratios of nitrate samples from the Aguas Blancas and Baquedano districts in the hyperarid core of the Atacama Desert (Fig. 1) range between $148.9 \pm 9.5 \times 10^{-15}$ and $1580 \pm 244.1 \times 10^{-15}$, but most of them are clustered within a narrow range, $~100–500 \times 10^{-15}$ (average $483.2 \pm 107.9 \times 10^{-15}$), deviating significantly from the pre-anthropogenic atmospheric value of $1500 \pm 150 \times 10^{-15}$ (Fig. 2; Table DR1 in the GSA Data Repository[1]). These significantly low ratios rule out a prevalent atmospheric/eolian source for most of the I and point toward an old I source (Fehn et al., 2007; Fehn, 2012). Our results are in close agreement with ^{129}I data from supergene enrichment zones of the giant Chuquicamata porphyry Cu deposit located ~100 km north east of the nitrate ore fields (Reich et al., 2013), strongly suggesting that the anomalous enrichment of I in the nitrates and in supergene Cu deposits shares a similar source.
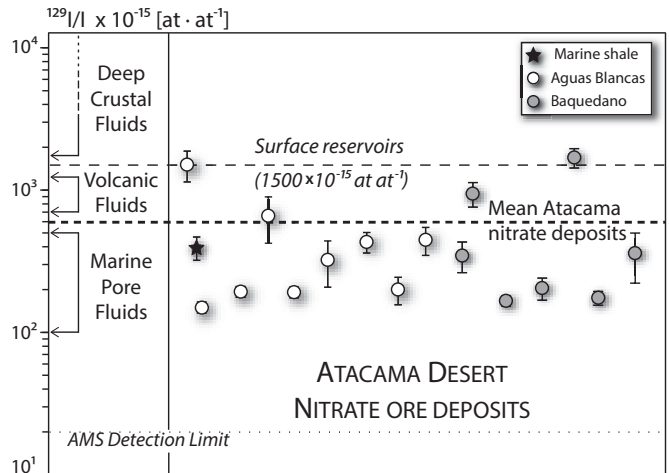
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[1]GSA Data Repository item 2014090, Table DR1 (iodine concentrations and isotopic ratios of nitrate samples) and Table DR2 (chromium concentrations and delta-chromium values of nitrate samples), is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 2. ^{129}I/I ratios of nitrate samples from Atacama Desert (northern Chile) (AMS—accelerator mass spectrometry). Left vertical axis shows ^{129}I/I ratios for different Earth reservoirs (Fehn et al., 2007). Error bars are shown for each ratio. Thick horizontal dashed line shows average ^{129}I/I ratio of the nitrates (483×10^{-15}), while light horizontal dashed line shows pre-anthropogenic surficial/atmospheric iodine ratios (1500×10^{-15}). White circles represent Aguas Blancas samples, and gray circles represent Baquedano samples. Black star shows ^{129}I/I ratio of Jurassic marine shales from Atacama Desert.

Considering that the cosmogenic signal is accumulated in fluids related to organic matter (e.g., marine sediments; Fehn et al., 2007), the low ^{129}I/I ratios ($~100–500 \times 10^{-15}$) reported here indicate that I was most likely leached from marine sedimentary rocks that form part of the Jurassic marine basin at the eastern border of the Atacama Desert (Vicente, 2006; Mpodozis et al., 2005) (Fig. 1), which can contain up to 90 ppm of I and show a distinct ^{129}I/I isotopic ratio of $~393.1 \pm 73.5 \times 10^{-15}$ (Fig. 2). The higher ^{129}I/I ratios ($~600–1580 \times 10^{-15}$) observed in a few samples are indicative of the influence of meteoric water with high pre-anthropogenic ^{129}I/I ratios, most likely related to infrequent moisture and flooding events associated with increased precipitation in the High Andes, and subsequent groundwater recharge episodes that occurred since the formation of the nitrate deposits (e.g., 16–10 ka) (Nester et al., 2007).

The aforementioned I signal detected in the nitrates is consistent with Cr stable isotope data (Fig. 3; Table DR2). All nitrate samples have positive $\delta^{53/52}$Cr$_{SRM979}$, within a range of +0.050‰ to +3.088‰ (average of +1.104‰), showing a strong enrichment in the heavier Cr isotope compared to the mean value of silicate Earth reservoirs (Fig. 3). The $\delta^{53/52}$Cr$_{SRM979}$ data for igneous and marine sedimentary rocks from the Atacama Desert are slightly negative as expected (−0.192‰ to −0.078‰), confirming that Cr isotopic fractionation involved in the Andean rock cycle is negligible. Cr in silicate Earth reservoirs is exclusively present in its trivalent oxidation state, Cr(III). It has been shown that Cr isotopes do not significantly fractionate during weathering and through oxidation from Cr(III) to Cr(VI) (Izbicki et al., 2008; Zink et al., 2010), while partial reduction of Cr(VI) to Cr(III) leads to isotopic fractionation in the per mil range on the ^{53}Cr/^{52}Cr ratio. Therefore, the highly fractionated Cr isotope signature of chromate components in Atacama's nitrates with respect to common Cr sources such as igneous rocks and marine shales is strong evidence of extensive Cr redox cycling from its source to the final deposition in the nitrates. Our nitrate $\delta^{53/52}$Cr data are comparable to groundwater $\delta^{53/52}$Cr values from the Mojave Desert (Izbicki et al., 2008, 2012), and it is important to note that efficient natural Cr isotopic fractionation has only been reported associated to Cr reduction in groundwater, where softer chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) bonds of the lighter Cr isotopes are preferably broken, enriching the residual Cr(VI) in groundwater in heavier Cr isotopes. Therefore,
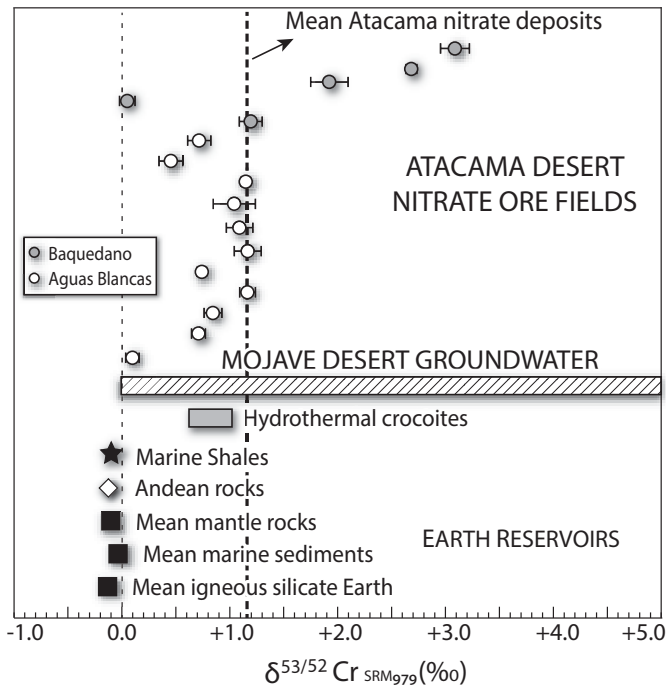
Figure 3. $\delta^{53/52}Cr_{SRM979}$ of nitrate samples from Atacama Desert (northern Chile). White and gray circles represent Aguas Blancas and Baquedano samples, respectively. Error bars are shown for each value. Mojave Desert (western USA) groundwater $\delta^{53/52}Cr$ values are displayed in hachured rectangle (Izbicki et al., 2008, 2012). Black star and white diamond show $\delta^{53/52}Cr$ value of Jurassic marine shales and igneous rocks from Atacama, respectively. Mean values for igneous silicate Earth, marine sediments, mantle rocks, and hydrothermal crocoites are shown for comparison (Schoenberg et al., 2008). Thick vertical dashed line shows average $\delta^{53/52}Cr$ value for nitrates (+1.104‰), and light dashed line represents 0.0‰ value.

we propose that Cr was leached as Cr(III) from its source upstream (e.g., Neogene volcanics and Jurassic shales in the Andes Mountains; Mpodozis et al., 2005), partially oxidized to Cr(VI), and released into groundwater that infiltrated westwards to the endorheic Central Basin, where decreasing dissolved O_2 conditions and the presence of Fe(II)-bearing minerals partially reduced and removed Cr from solution leaving a progressively heavy $\delta^{53/52}Cr$ signature downstream (Ellis et al., 2002). Within this framework, it is noteworthy that some previously reported non-marine values of sulfate and non-atmospheric nitrogen signatures of oxygen in the nitrate deposits (Böhlke et al., 1997; Rech et al., 2003; Michalski et al., 2004) are indicative of the various chemical inputs along the flow path, i.e., terrestrial sulfate from magmatic/geothermal fluids and sedimentary nitrogen contributions by microbial fixation in soils, into groundwater.

Our data provide new insights toward the understanding of the genesis of the enigmatic nitrate deposits of Atacama. Both $^{129}I/I$ ratios and $\delta^{53/52}Cr$ values point toward the important and previously unforeseen role played by groundwater during leaching and transport of the exotic I and Cr chemical components found in the Atacama nitrates. Based on our results and previously published O, N, and S stable isotope data, we propose an integrated, multi-source genetic model that explains the occurrence of all components found in the nitrate deposits and is consistent with the geological, hydrologic, and climatic evolution of this region (Fig. 4). Our model involves leaching of I and oxidized Cr from sedimentary rocks and volcanic sequences in the High Andes, which were then transported westwards along with other chemical species to the Central Basin by groundwater. Neogene climate change and tectonic uplift resulted in decreased precipitation rates from >200 mm/yr to <20 mm/yr between ca. 20 and 10 Ma, and to <3 mm/yr today in its hyperarid core (Hartley and Chong, 2002; Reich et al., 2006, 2009; Amundson et al., 2012). This led to the development of an exclusively endorheic drainage system recharged in the High Andes (Magaritz et al., 1990), where increase in elevation of the Andean plateau due to uplift in the late Miocene (Allmendinger et al., 1997; Garzione et al., 2008) would also have increased the hydraulic
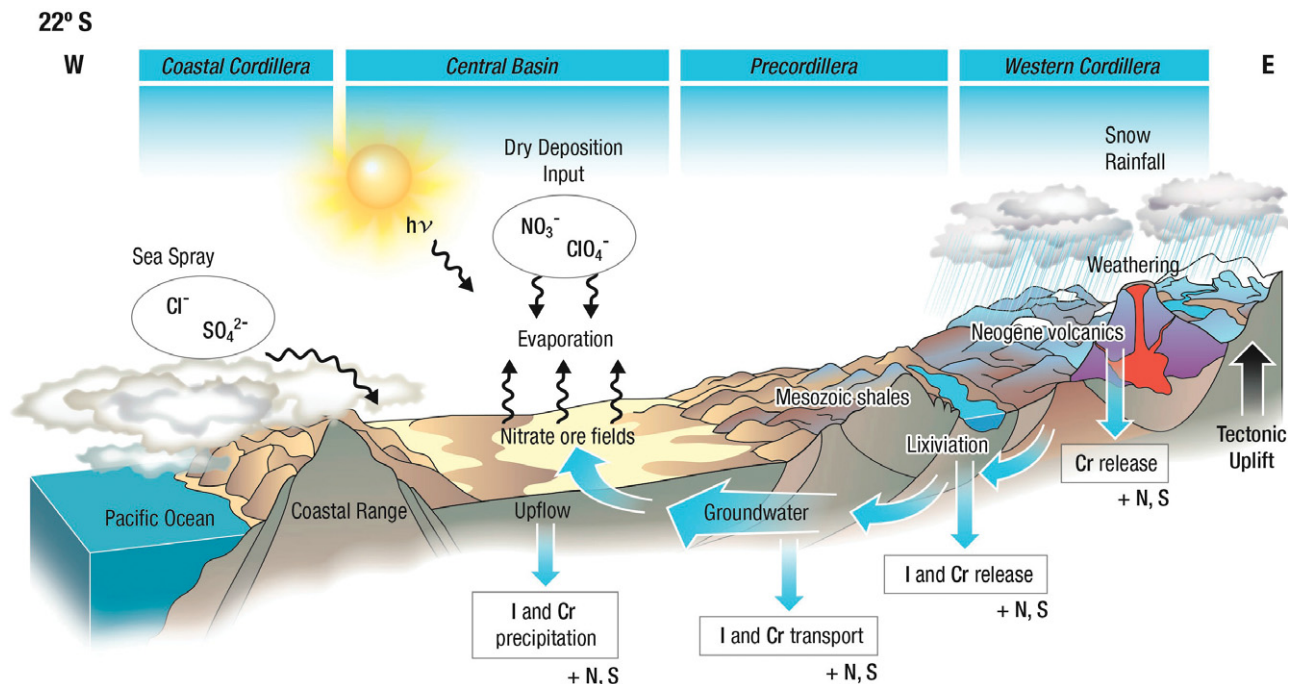

Figure 4. Multi-source genetic model for the formation of Atacama Desert's giant nitrate deposits. West-east section at latitude 22°S shows main structural domains: Coastal Cordillera, Central Basin, Precordillera, and Western Cordillera. Processes involved in formation of nitrate deposits are shown, i.e., atmospheric dry deposition, groundwater transport and precipitation, sea spray inputs, and evaporation. I—iodine as iodate (IO_3^-) or iodide (I^-); Cr—chromium as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or Cr(III); S—sulfur as sulfate (SO_4^{2-}); N—nitrogen as nitrate (NO_3^-). Perchlorate (ClO_4^-) and chloride (Cl^-) are also shown.

potential between the wet Altiplano and the dry western slope, creating favorable conditions for increased groundwater flow toward the Central Basin (Hoke et al., 2004). The precipitation of iodate and chromate minerals (and probably some sulfate and nitrate) was favored downstream in the Central Basin by an "impermeable" barrier effect of the eastern slope of the Coastal Range (>1000 m above sea level at 10 Ma; Allmendinger and González, 2010) that allowed saline and reduced groundwater to efficiently rise, evaporate, and oxidize in the presence of a continuous dry deposition flux of atmospheric nitrate and perchlorate, and excursions of sulfate and/or chloride-bearing sea spray from the Pacific Ocean (Fig. 4).

CONCLUDING REMARKS

We conclude that the large and almost continuous, ~700-km-long by ~20-km-wide belt of nitrate deposits of Atacama represent an unusual convergence of common physical-chemical processes with an ideal geologic, tectonic, hydrologic, and climatic setting that is specific to Atacama—that is, a convergent margin section undergoing rapid uplift since the late Miocene to elevations sufficient for exhumation and weathering of Jurassic marine sequences, and enhanced large-scale groundwater flow toward the Central Basin. The critical trigger for the formation of Atacama's nitrate deposits was the concomitant increase in tectonic uplift and desiccation that allowed not only the precipitation of transported species from uprising groundwater in the Central Basin due to evaporation, but also the long-term accumulation and preservation of atmospheric nitrate.

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