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Strontium Isotope Systematics of Tenerife Wines (Canary Islands): Tracing Provenance in Ocean Island Terroir

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Abstract: The production of fraudulent goods remains widespread and economically damaging. The high value of the wine industry makes it particularly vulnerable, and a number of geochemical methods have been developed to ensure traceability and identification of origin. Here, strontium (Sr) isotope data on wines from five defined regions in Tenerife (Canary Islands, Spain) show that the young volcanic geology imparts a clearly identifiable low $^{87}Sr/^{86}Sr$ signature (<0.7072). These values discriminate Tenerife wines from mainland Spanish and continental European produce, as these are much more radiogenic in general. However, unlike continental wine regions, wines from Tenerife show small but ubiquitous enrichments in $^{87}Sr/^{86}Sr$ above what is expected in the soils. Bentonite addition has not affected the $^{87}Sr/^{86}Sr$ signatures, with white wines at lower Sr concentrations than red wines in all regions. A number of natural contributions to the terroir are evaluated in relation to Tenerife's unique combination of geology and geography. Atmospheric precipitation (rainfall) is likely a dominant influence on Sr isotope systematics in northern Denominación de Origen regions, and evaporation may play a role in buffering signatures in southern regions. Other natural additions of ^{87}Sr are not precluded at a local scale, given the large range in climatic conditions of island terroir and known input of mineral dust from Africa. Despite natural explanations affecting the overall small shift observed, there are clear outliers with considerably higher $^{87}Sr/^{86}Sr$ and Sr concentration. This confirms the utility of Sr isotope systematics for oceanic-island viticulture and demonstrates the use of young volcanic soils for tracing natural inputs that may be masked in other regions.

Keywords: Sr isotopes; geographic traceability; ocean-island viticulture; geology and wine authentication; wine provenance; oenological database

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1. Introduction

The traceability and authenticity of the highest quality agricultural products in Spain is important, as fraudulent goods are widespread, e.g., wine, cheese, olive oil, honey, tomatoes, cacao, meat, etc. Strict regulations are in place, both at the European level (Regulation (EU) No 1308/2013) and at the country level (e.g., Spain: Real Decreto 774/2014), in order to provide robust regional quality controls. The application of a Denominación de Origen (DO) label allows for regional characterisation of specialised agricultural products and a framework for geographic traceability methods. The provenance of wine holds particular interest because the DO label bestows a level of desirability and influences sale prices. Spain, Italy and France together produce around half of the world's wine (47% in 2014 [1]), with Spain alone exporting nearly 2 billion litres worth EUR 2 billion in 2018 [2]. The high value of the wine industry makes it vulnerable to forgery, with the European sector reporting direct losses of 2.3% or ~EUR 531 million in 2016 [3]. Fraudulent wine sales in Spain accounted for ~EUR 90 million of that loss.

Trace and rare earth elemental studies distinguishing wine provenance have been applied to wine tracing around the world [4–8]. Elemental and stable isotope studies, e.g., $\delta^{18}O$ and $\delta^{2}H$, are used by the International Organisation of Vine and Wine (OIV) to identify forgery and to produce standardised analytical methodologies. However, elemental studies require a wide-ranging correlative approach and concentrations vary between grape types, while stable isotope ratios are significantly affected by climatic conditions in a given vintage [9,10].

Several radiogenic isotope systems have proven useful in authentication studies [11–16]. Strontium (Sr) can be considered the most robust for several reasons. Mass-dependent fractionation between ^{87}Sr and ^{86}Sr does not take place as the metal moves from soil $\rightarrow$ vine $\rightarrow$ wine [17] or during wine processing [18,19]. The ratio of $^{87}Sr/^{86}Sr$ does not change between vintage years [20]. $^{87}Sr/^{86}Sr$ remains a reflection of the soil and bedrock region upon which the grapes are cultivated and does not vary by grape type, unlike lead isotopes [8]. It follows that regional geology can be used as a predictor of Sr isotopic signature anywhere in the world, though it is important to test for Sr available to the vine (bioavailable) in order to develop large-scale comparable databases. The approach has been successfully, applied and Sr isotope prediction maps and 'smart' tools in wine regions susceptible to fraud are available, e.g., Lambrusco wines from the Modena district, Italy [21]. $^{87}Sr/^{86}Sr$ mapping is also a tool widely used in archaeology, particularly for tracing movements of populations through diet [22].

In this contribution, the Tenerife wine industry is presented and Sr parameters for the five DOs are defined. An assessment of the viability of using $^{87}Sr/^{86}Sr$ as a provenance indicator is made, including whether common processing additions (e.g., bentonite) are evident in the provenance signature of white wines. The rare combination of Tenerife's geology and geography offers a valuable opportunity to investigate natural Sr contribution pathways from source(s) to bottle.

1.1. Sr Isotopes in Nature

Strontium is one of the alkaline earth metals, which are generally found in nature as cations with a +2 valence. Sr is reactive, and since it can readily substitute for other alkali earth metals (most commonly, calcium), it is mobile in the natural environment. Sr is a minor-trace element in rocks and surface deposits and can also be found in minerals, soils and clays, e.g., sulfates, carbonates, feldspars and smectite [23]. Sr has 4 stable (non-radioactive) isotopes: ^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr. Of interest to provenance studies is the ratio between ^{87}Sr and ^{86}Sr because radiogenic ^{87}Sr is produced through decay of the long-lived isotope ^{87}Rb (half-life 4.7×10^{10} years). Therefore, a geographic environment has an $^{87}Sr/^{86}Sr$ signature that reflects its initial Sr plus that which is added through Rb to Sr decay. Sr isotopes are particularly useful in agricultural provenance studies because they are not fractionated from each other by biogenic or other low temperature alteration processes due to their small mass differences compared with their high atomic masses [24].

In soils, Sr is available as part of the bio-available or leachable fraction [23]. The ratio of ^{87}Sr to ^{86}Sr taken into a root system is a direct reflection of the soil system ratio, which is derived from a number of factors. The primary influence is the sub-stratum, which on the island of Tenerife (Canary Islands) is limited to young (<13 myr) volcanic rocks of basaltic and phonolitic composition [25,26]. Vineyard bedrock is generally (although not exclusively) formed of very young strata (<1.57 Ma [27]) because most of the islands surface is defined by the addition of volcanic material. $^{87}Sr/^{86}Sr$ in Tenerife basaltic bedrocks ranges from 0.70284 to 0.70426 (n = 110 [28]). The phonolites (more silicic) range from 0.70284 to 0.70571 (n = 39 [28]) and with markedly lower Sr concentrations: average ~280 ppm compared with ~920 ppm in Tenerife basalts. The attendant low $^{87}Sr/^{86}Sr$ in bedrock and soils are a reflection of the lack of time for ^{87}Sr ingrowth above the original ^{87}Sr/^{86}Sr at the time of extraction (melting, ascent and eruption) from the mantle reservoir.

Secondary natural sources of Sr include sea-spray and atmospheric deposition (in the form of precipitation, dust, fertiliser and pollution). Rainfall in oceanic island settings often has high ^{87}Sr/^{86}Sr, similar to seawater (~0.710) but at much lower Sr concentrations [23]. Precipitation in the Canary Islands can also contain a uniquely high quantity of dust derived from the southern Morocco Sahara desert [29], with ^{87}Sr/^{86}Sr around 0.72212 [30]. These secondary inputs are highly variable over comparatively short distances due to the steep-sided and isolated location of Tenerife, which is situated in a trade wind belt. Subsequent to natural inputs, irrigation, fertilizers and wine processing techniques have the potential to modify ^{87}Sr/^{86}Sr signatures.

1.2. Viniculture in Tenerife

The wine industry in Tenerife is well-established, dating back to the 15th century. The Canary Islands are known for grape varietals that were decimated in other countries by the phylloxera insect [5]. Perhaps the best-known Canarian varietal is the Malvasía grape. The combination of old, ungrafted vines, traditional, non-mechanised methods and unusual flavours due to variable topography, microclimate and volcanic soils have garnered Tenerife wine respect in the global market (c.f. USA [31], UK [32], and other sommelier publications available in print and online) and is a significant tourist draw. The value of exports has increased rapidly in the last decade (Figure 1) to EUR 4.9 million by the end of the 2018/2019 reporting period [33], despite litres of wine produced remaining relatively constant.

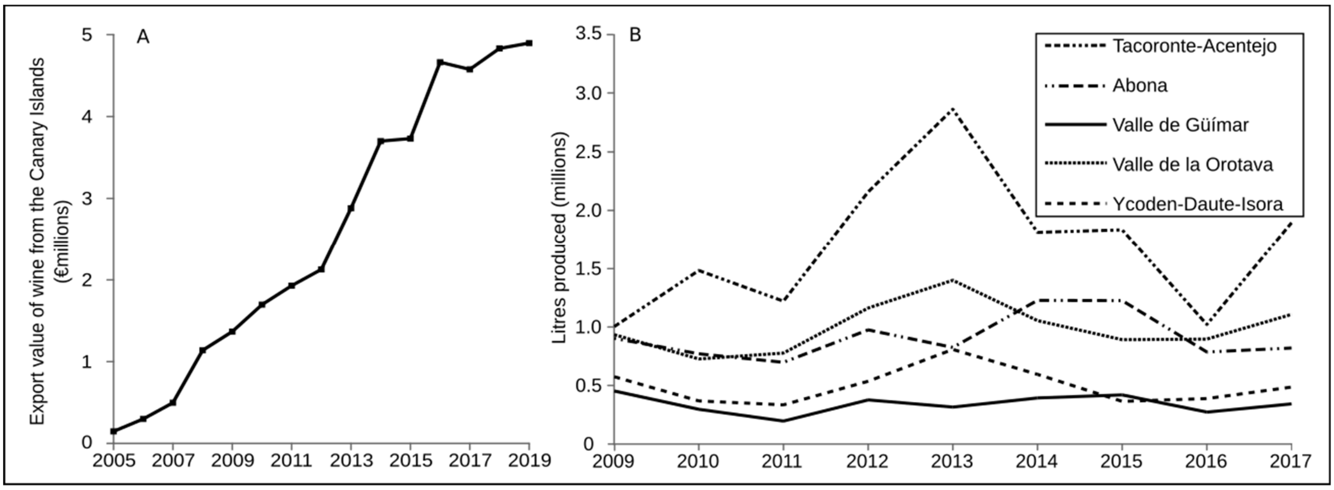

Figure 1. (**A**) The rise in revenue generated by the export of wine from the Canary Islands [33]. (**B**) Reported wine production figures for the Tenerife Denominación de Origens [34].

The island of Tenerife is divided into five wine regions, labelled "Denominación de Origen" (DOs; Figure 2), with boundaries defined by principle landforms and aspect. A total of 2508 ha of vineyard are included in the defined DOs, shared between 4581 wine-growers [2]. A sixth "DO Tenerife" label was introduced in 2017, allowing island-wide co-operatives to combine their produce, having the effect of reducing waste and allowing smaller growers to participate in the market while still adhering to the high standards required for DO status. The cross-island label "VC Canarias" was created for similar reasons, with less stringent standards, while still providing a high level of quality assurance. Each of the five Tenerife DOs can be distinguished by differences in climatic conditions due to trade wind influence and orography, meaning different grape varieties perform better in different regions (Table 1).

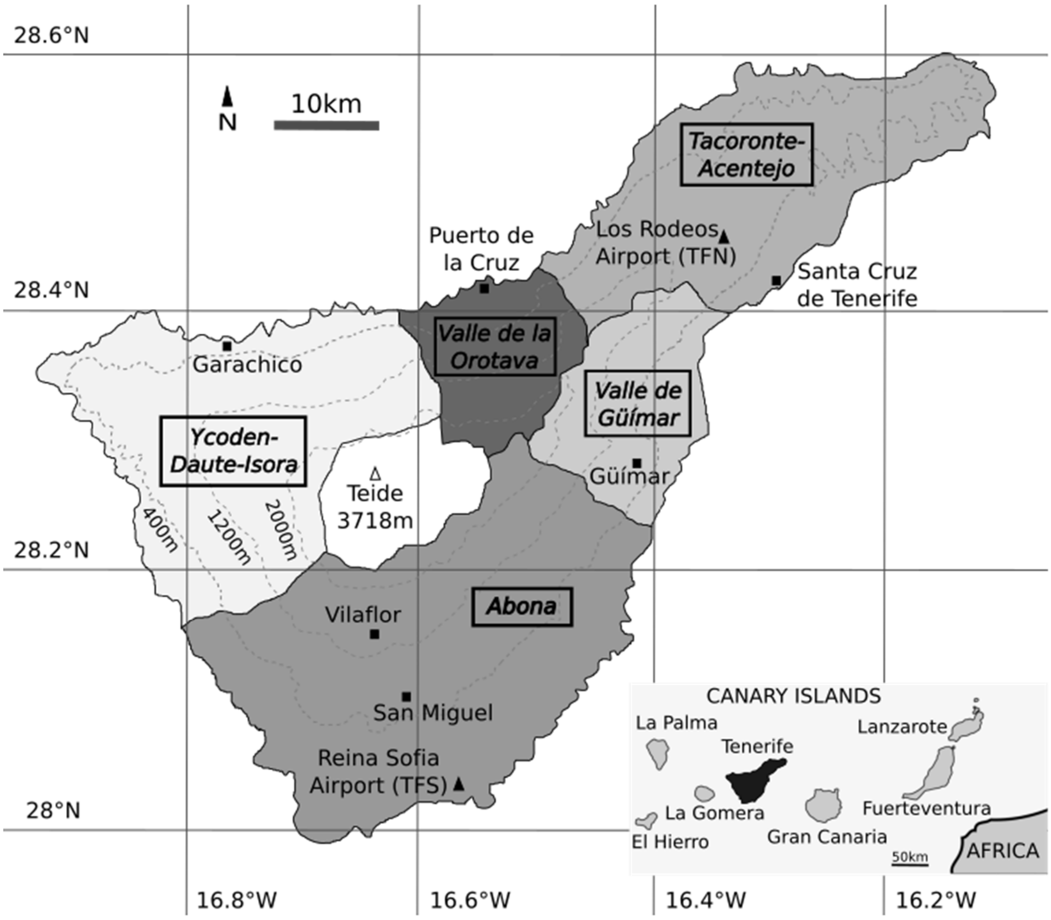

Figure 2. The island of Tenerife, Canary Islands (see inset), and the geographical boundaries of the five Denominación de Origen regions (DOs). Towns (squares) and geographical landmarks (triangles) in each are labelled.

Vineyards are located on variable terrain ranging from sea level to ~1700 m, and each DO consists of several micro-climates. Wines with the DO label are comprised exclusively of grapes grown on land belonging to the Bodega (wine-house), within the DO boundaries set out by the agricultural department of the Tenerife government. In general terms, vineyards at lower elevations are likely to have a greater clay component to the soil, whereas higher elevation vines may grow on poorly developed, rockier soil. All vineyard soils are derived from young volcanic rocks. These are either developed on basaltic or phonolitic lava flows or, more typically, on sandy soil termed 'jable', which is derived by the breakdown of volcanic ash and other pyroclastic deposits. Vineyards are often managed by hand due to the steep, small terraced nature of plots and employ rare traditional methods such as the braided cord (vine braids can reach 15 m in length) and vines grown onto trellises shading other terraced crops.

Table 1. Size, geography, varietals and economic contribution of each wine according to Denominación de Origen (DO) on the island of Tenerife [2,33,35,36].

Denominación de Origen (Area of Vineyards, Ha)	Area (Ha) and % of Total Coverage	Municipalities Included	Altitude Range of Vineyards (m)	White: Red Grapes	Dominant White Varietals	Dominant Red Varietals	Market Contribution 2017/2018 (EUR Millions) and Percent of Total
Abona	852 (34.0%)	Granadilla de Abona, Arico, Adeje, Arona	400–1700	80:20	Listán Blanco, Malvasía, Marmajuelo	Listán Negro, Negromoll, Tintilla	3.5 (24.9%)
Valle de Güímar	165 (6.6%)	Güímar, Arafo, Candelaria	100–1500	62:38	Listán Blanco, Malvasía, Moscatel, Gual, Verdello, Sabro	Listán Negro, Negromoll, Cabernet Sauvignon, Merlot, Pinot Noir, Shiraz, Temperanillo	1.02 (7.3%)
Tacoronte-Acentejo	1016 (40.5%)	Tacoronte, Santa Ursula, Tegueste, La Matanza, La Victoria, El Sauzal, La Laguna, El Rosario, part of Santa Cruz	100–1000	6:94	Listán Blanco, Malvasía, Moscatel, Gual, Verdello, Vijariego	Listán Negro, Negromoll	5.75 (40.9%)
Valle de la Orotava	317 (12.6%)	Los Realejos, La Orotava, Puerto de la Cruz	250–800	50:50	Listán Blanco, Malvasía, Marmajuelo, Albillo Moscatel, Gual, Sabro, Verdello, Vijariego	Castellana Negra, Listán Negro, Negromoll, Tintilla, Malvasía Rosada	2.58 (18.3%)
Ycoden-Daute-Isora	158 (6.3%)	Buenavista del Norte, El Tanque, Garachico, Guía de Isora, Icod de los Vinos, Los Silos, San Juan de la Rambla, La Guancha, Santiago del Teide	50–1400	70:30	Listán Blanco	Listán Negro, Negromoll	1.21 (8.6%)

2. Materials and Methods

2.1. Wine Collection

A sample set of 101 wines was investigated for Sr concentrations and isotopic ratios (Table 2). Ninety two samples were provided by the Laboratorio Insular de Vinos de Tenerife, with vintages from 2013–2016. Nine more were collected as part of a more targeted approach to the five Denominaciónes de Origen, all with a vintage of 2018. Samples were provided as either finished, corked bottles or decanted from fermenting tanks at the Bodega (cellar door) into acid-cleaned HDPE 200 mL bottles. Samples were stored in a dark, constant cool temperature location until processing.

Table 2. Summary of wine samples per DO.

Location	Number of Samples	Red/White/Rosé
DO Abona	13	7/4/2
DO Tacoronte-Acentejo	12	6/4/2
DO Valle de la Orotava	8	4/3/1
DO Valle de Güímar	8	2/4/2
DO Ycoden-Daute-Isora	8	4/4/0
DO Tenerife	22	11/10/1
VC Canarias	10	3/6/1
Guachinches (Tenerife, no DO, small batches)	10	8/2/0
Peninsular DOs	10	4/5/1

2.2. Isotopic Analyses—Equipment and Reagents

All sample processing for isotopic analysis took place inside a clean space under positive pressure using filtered (ULPA filters), air-conditioned air. Suprapure (SPa) and ultrapure (UPa) concentrated HNO_3 (15.1 M), HCl (10.4 M), H_2SO_4 (17.5 M) and H_2O_2 (9.7 M) were purchased directly from Romil Acids. Ultrapure water (18.2 MΩ cm) was obtained from a Merck Millipore Milli-Q® system when required (hereafter termed MQ). All acid dilutions were prepared using these reagents in pre-cleaned teflon bottles. Savillex PFA vials, labwear and teflon tubing were used throughout. All labwear was pre-cleaned in alternating 50% HNO_3 and HCl acids and rinsed several times with MQ. Sr isolation was achieved using disposable cation-exchange resin specific to Sr (Eichrom®, SR-B50-S Triskem International), which was sequentially pre-cleaned using UPa acids. Resin was loaded into pre-cleaned pure quartz columns and then underwent a final sequential acid clean before sample loading. Sr-spec resin is especially useful for separating Sr from Rb and Ba, which are the most important sources of mass interference when measuring isotopic Sr. The international standard NIST SRM 987 SrCO3 was prepared in 2 M UPa HNO_3 and stored in a PFA sealed container, before being processed using the same methodology as the samples. Procedural blanks, using MQ water as mock sample, were used for quality control within each batch of 20 wine samples.

2.3. Isotopic Analyses—Purification of Sr

Wine sample digestion followed the methodology approach of Marchionni et al. [15] with the aim of decomposing organic matter within the sample. All digestion and column work were conducted under clean laboratory conditions. Five millilitres of wine were gently dried at 60 °C (being careful not to burn the residue) under a closed sample vessel system, using teflon tubing to waft ULPA filtered air across the sample, until a gel residue remained. Next, breakdown of organic matter was achieved using 2 mL 19.4 M UPa H_2O_2 and a drop of UPa HNO_3 on a hotplate at 40–50 °C for 24 h. If the sample still contained particles or had a very strong colour (common in red wine samples), this step was repeated after a dry-down cycle. Subsequently, 2 mL UPa HNO_3 was added and heated with the vessel lid on for 24 h at 110 °C. For samples still retaining colour (and therefore organic matter), the mineralisation step with H_2O_2 was repeated until the sample was clear. The sample was then dried slowly to nitrate salts and stored until ready to load onto ion separation columns.

Column work followed the method of Pin et al. [37]. The digested wine sample (nitrate salts) was redissolved in 1 mL 2 M UPa HNO_3 and loaded in three aliquots onto ~83 mg of pre-conditioned resin. After complete draining of the initial sample load, the Sr-spec resin in the column was washed with 4 × 500 µL UPa 7 M HNO_3 to remove Ba (and other matrix elements), allowing complete drainage between washes. Sr was subsequently recovered from the resin using 4 × 500 µL of MQ water. The resulting sample was gently dried, re-nitrified with concentrated UPa HNO_3 to break down any remaining organic components, re-dried and stored for loading on the TIMS.

2.4. Isotopic Analyses—Instrumentation and Measurement

Purified Sr was redissolved in 1–2 µL of the $TaCl_5$ activator solution and loaded onto previously degassed Re filaments. The samples were dried slowly and 'flashed' at 2 Amps to burn off any remaining ^{87}Rb. The filaments were loaded as double assemblies onto the source wheel. Two filaments per wheel (21 positions) were loaded with the standard reference material NIST 987 (processed through resin columns alongside samples) and measured regularly to monitor machine performance throughout analysis (Supplementary Material Table S1).

Sr and Rb isotope abundances (^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr; ^{87}Rb and ^{85}Rb) were measured using a Thermo FinniganTM Triton Plus Thermal Ionisation Spectrometer (TIMS), equipped with an RPQ lens for maximum sensitivity. The ITER TIMS also features a virtual amplifier, which allows for rotation of the amplifiers measuring the ions arriving in each Faraday cup, maximising precision by cancelling out errors in gain calibration factors. Measurements were obtained in multidynamic (peak-jumping) mode over 120 cycles. Rb and Kr mass interferences were corrected for, followed by exponential normalisation to $^{88}Sr/^{86}Sr$ 8.375209. Six blocks of 20 measurements were collected (allowing each amplifier to measure each isotope) with 8.389 s of integration time. The idle time was set to 3 s to eliminate potential memory effects on the cups.

Procedural blanks contained 125–332 picograms of Sr (*n* = 7; Supplementary Material Table S2), insignificant compared with the sample loads. The Sr signals were measured once ^{88}Sr reached > 2 volts (more commonly > 6) for 6 blocks of 20 measurements. One sigma error margin was 10^{-5}.

2.5. Isotopic Analyses—Laboratory Collaboration

Wine samples were analysed for Sr isotopes at two institutions: University of Aveiro (Portugal) and the Instituto Tecnológico y de Energías Renovables (ITER), Tenerife, Canary Islands (Spain). The analytical methods used at the established University of Aveiro laboratory are presented in Supplementary Material Table S3; see also Ribeiro et al., 2014 [38]. The analysis from two institutions permitted validation of the results obtained in a new laboratory at ITER: cross-analysed samples are presented in Supplementary Material Figure S1. The analyses confirm that the TIMS facility at ITER, Canary Islands, can be considered fit for our purpose.

2.6. Trace Element Analyses

Metals and other trace element concentrations were measured using a ThermoScientific iCAP Q inductively coupled plasma mass spectrometer (ICPMS) coupled with Qtegra software. Before each analytical run, the instrument was calibrated and tuned until accurate and stable using purpose-developed solutions purchased from Thermofisher. Perkin-Elmer multi-element standard solutions were gravimetrically prepared in concentrations ranging from 1 ppb to 1 ppm to bracket the Sr concentrations anticipated from the samples. These standard solutions were measured at the start and end of the analytical runs. The limits of detection reported by the software ranged between 0.04–0.14 ppb, although in reality, standard deviations on measurements < 1 ppb became higher than 10%. An internal standard of 15 ppb rhodium was used to monitor the machine performance and sample uptake. Wine samples were diluted gravimetrically 20 times with MQ water to bring Sr concentrations into the range of bracketing standard solutions. The ICPMS system was equipped with a Cetac ASX-520 autosampler, peri-staltic sample delivery system, PFA nebuliser, cyclonic spray chamber and nickel cones. Sample analyses were conducted in quantitative KED measurement mode, with each analysis comprising 5 sequences of 20 sweeps at 0.35 s each and the dwell time being 0.01 s between sweeps. The percent RSD values per sample analysis are given with the results in Supplementary Material Table S4.

3. Results

Sr concentrations and $^{87}Sr/^{86}Sr$ for all (anonymised) samples in this study are provided in Supplementary Material Table S4 and summarised in Figures 3 and 4.

The minimum Sr concentration is similar in wines from across the five DO regions of Tenerife (~500 ppb) and in the collective DO Tenerife and VC Canarias denominations. Tenerife wines fall within a restricted range of isotopic values (0.7040–0.7085), and the mean $^{87}Sr/^{86}Sr$ of all DO regions is below 0.707 (Figure 3A). However, variations are apparent in relation to the geographic location of the individual DOs (as defined in Figure 2). Unless otherwise highlighted, the following treatment of data and discussions refer only to these five individual geographic regions, as wines under DO Tenerife and VC Canarias can use grapes from all regions.

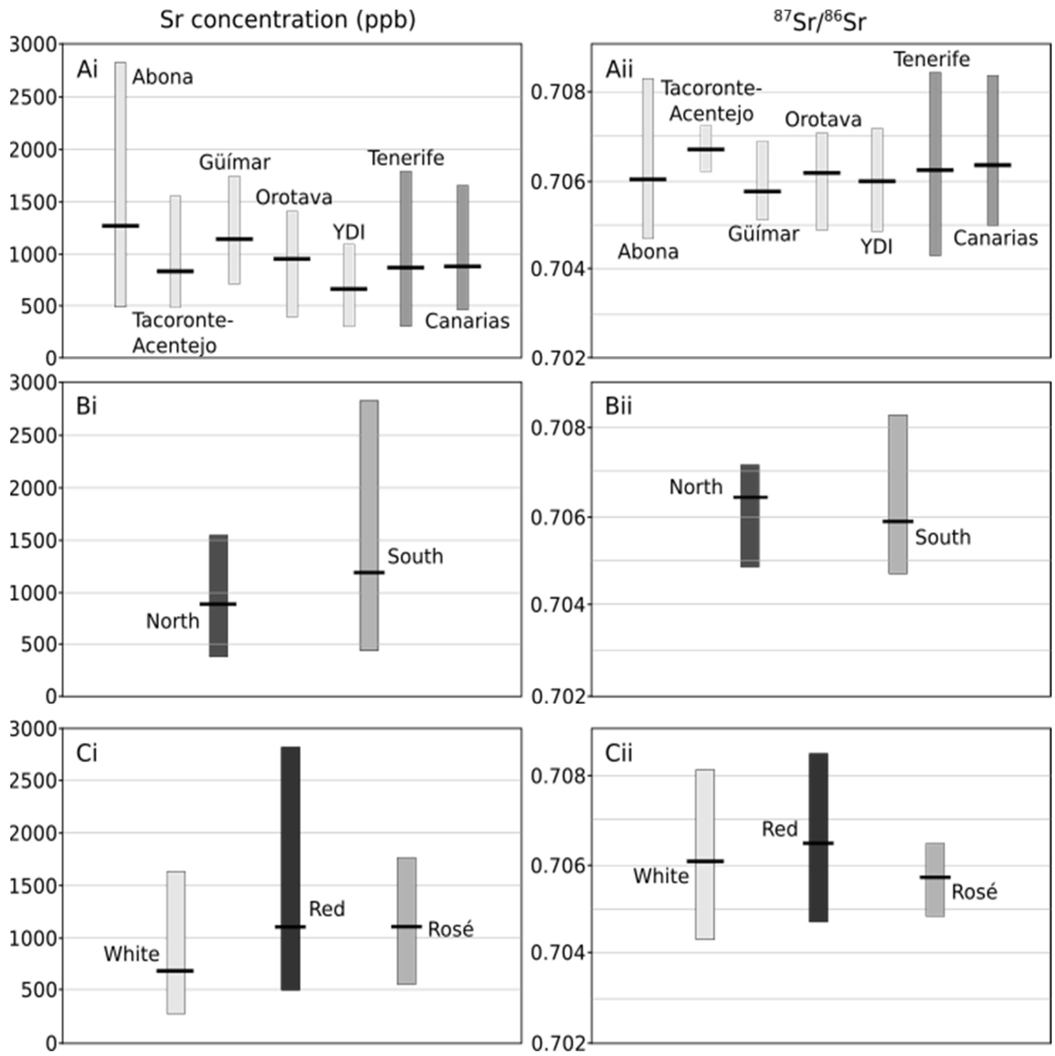

Figure 3. Sr characteristics of Tenerife wines according to (**A**) Denominación de Origen (and the VC label of Canarias, (**B**) north/south region, (**C**) and wine type, with the concentrations (**i**) and isotopic ratio (**ii**) of each category.

DO Abona and Valle de Güímar, in the south of Tenerife, have higher minimum and maximum Sr concentrations (Figure 3A; 490–2827 ppb) than the northern DOs (Valle de la Orotava and Tacoronte-Acentejo; 402–1541 ppb). Southern wines also have higher mean Sr concentrations coupled with lower mean $^{87}Sr/^{86}Sr$ (Figure 3B). White varietals typically contain 400–600 ppb less Sr than their red counterparts in every DO; the mean Sr concentrations of DO-labelled white wines is 704 ppb, while reds are higher at 1124 ppb (Figure 3C). The valle de Güímar and Abona regions (dominantly white wine producers) have lower $^{87}Sr/^{86}Sr$ in whites than reds, while Tacoronte-Acentejo and Valle de la Orotava have higher $^{87}Sr/^{86}Sr$ in white wines (Table 3, Supplementary Material Table S4). All white wines from DO labels have $^{87}Sr/^{86}Sr < 0.7072$ ($n = 19$), whereas several red samples exhibit ratios up to 0.7085 (Figure 3C, discussed later).

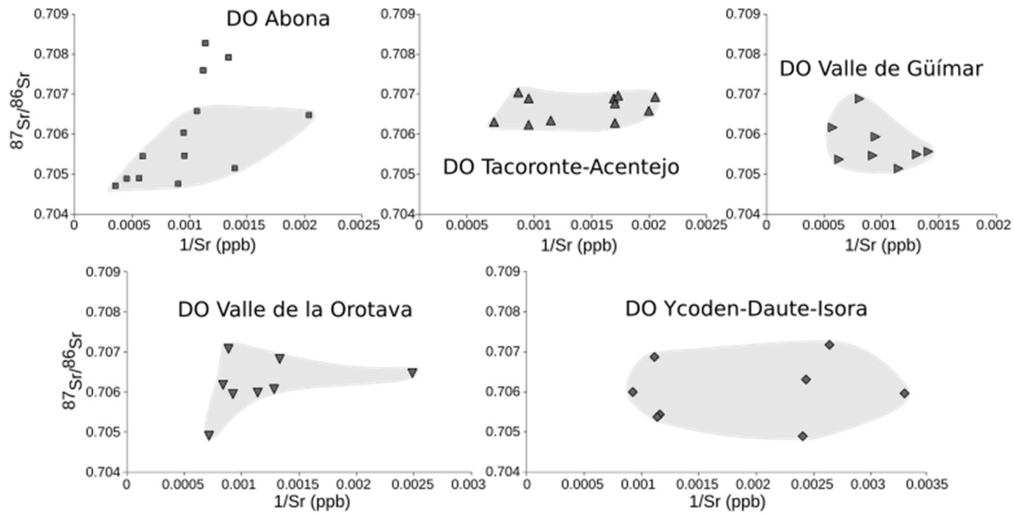

Figure 4. Sr isotope and concentration fields for wines from the five regional Denominación de Origens of Tenerife. Note that the Sr concentration scale varies between DOs. The three samples outside the field indicated in DO Abona are discussed in Section 4.5. Symbols represent wine samples in each DO.

Table 3. Mean isotopic and elemental Sr by Denominación de Origen and wine type in Tenerife (individual sample data can be found in Supplementary Material Table S4).

	Mean $^{87}Sr/^{86}Sr$	**Mean Sr (ppb)**	**Sr Min (ppb)**	**Sr Max (ppb)**
DO Abona	**0.70602**	**1260**	**490**	**2827**
Red wines	0.70649	1455		
White wines	0.70561	843		
DO Tacoronte-Acentejo	**0.70670**	**819**	**487**	**1541**
Red wines	0.70677	917		
White wines	0.70682	538		
DO Valle de Güímar	**0.70577**	**1130**	**710**	**1738**
Red wines	0.70653	1487		
White wines	0.70553	929		
DO Valle de la Orotava	**0.70621**	**952**	**402**	**1397**
Red wines	0.70605	1122		
White wines	0.70648	782		
DO Ycoden-Daute-Isora	**0.70600**	**654**	**304**	**1081**
Red wines	0.70592	931		
White wines	0.70608	378		
DO Tenerife	0.70625	855	304	1788
VC Canarias	0.70633	877	460	1642
Guachinches	0.70670	965	409	1587

Comparing wines from individual DO regions illustrates the Sr isotope variability within Tenerife. Four of the five DO regions do not exceed $^{87}Sr/^{86}Sr > 0.7072$ (Figure 4), and their means are all below 0.707 (Table 3). Valle de Güímar wines have the lowest $^{87}Sr/^{86}Sr$ (mean < 0.706) coupled with a small range and high relative mean Sr concentration (>1 ppm; Figure 3). DO Abona, adjacent to DO Valle de Güímar in the south, reaches even higher

Sr concentrations, up to 2827 ppb and the highest mean of all the DO labels (1260 ppb). $^{87}Sr/^{86}Sr$ in three samples from DO Abona exceed the maximum recorded in other DOs from Tenerife (Figure 4). The lowest mean Sr concentrations are found in wines from Valle de la Orotava and Tacoronte-Acentejo labels and are coupled with the highest mean values of $^{87}Sr/^{86}Sr$ (Figure 3 and Table 3). Tacoronte-Acentejo wines also have the most restricted range in isotopic values over variable Sr concentrations (Figure 4). The western Ycoden-Daute-Isora DO reaches very low Sr concentrations, with similar $^{87}Sr/^{86}Sr$ to other DO regions (Figure 4). Wines under the broad DO Tenerife and VC Canarias labels as well as samples from guachinche restaurants (non-DO designated establishments limited to selling wine from their own winery) span the elemental and isotopic compositions of the five distinct island DOs. This is expected, since these labels are produced from blending grapes from different regions.

4. Discussion

4.1. Anthropogenic Inputs—Farming, Clearing and Ageing Wines

Regional differences in Sr parameters are seen between DOs. These need to first be considered in terms of anthropogenic inputs during farming and post-processing of wines. Common agricultural practices such as lime addition and the use of fertilizers have the potential to modify $^{87}Sr/^{86}Sr$ signatures. These practices are common when soils are acidic and/or nutrient deficient. However, the advanced age of many vine plantations on Tenerife can mean root systems up to 20 m deep, while fertilizer input affects only the upper tens of centimetres of the soil horizons [39]. Tenerife's volcanic soils have abundant macronutrient contents (Ca, Mg, Na and K), which in combination with a low-yield crop (vines) and traditional runoff-capture techniques utilised [40], means soils do not become nutrient deficient even over decadal timescales.

Wine processing is another source of potential isotopic modification agents, e.g., nanofiltration to reduce the ethanol content, the addition of bentonite (a smectite clay) to 'clear' wines of proteins and ageing in wood barrels for flavour enhancement [18,41,42]. Multiple studies of these techniques have concluded that the isotopic signature is preserved throughout the process, from soil to grape through to the finished product. This is reinforced in Tenerife DO wines. Bentonite fining agents have high Sr concentrations, e.g., 59 ppm [41], and are added to white wines, so they may show a clay influence in their Sr signatures. Tenerife white wines have lower Sr concentrations (generally < 1 ppm and smaller ranges) than red wines in all five DO regions. 'Clearing' do not affect the Sr parameters, and regional differences in isotopic composition remain despite bentonite additions. Storage and ageing in wood barrels have been shown to very slightly increase Sr concentrations (around 10 ppb in 3 months) yet not modify $^{87}Sr/^{86}Sr$ values over the same time period [42]. Wines preserve their inherited $^{87}Sr/^{86}Sr$ signatures despite enhancement techniques.

4.2. Comparisons with Other Wine Growing Regions

The $^{87}Sr/^{86}Sr$ signatures in Tenerife DO wine samples are distinctly lower than that in all other principal wine-growing regions around the world (Figure 5). This is a direct consequence of the geology and the age of the substratum in each region. Old cratonic continents such as South Africa, Canada, China and Argentina produce wines with $^{87}Sr/^{86}Sr$ signatures averaging over 0.710. Some cratonic parts of Europe produce wines with even higher $^{87}Sr/^{86}Sr$, e.g., Romania and areas of Portugal, averaging 0.715. Therefore, Tenerife wines, with an average $^{87}Sr/^{86}Sr$ of ~0.706, can be readily distinguished from both mainland Spain (average ~0.709), European and global wines, and this near-unique provenance can be determined solely based on measurements of the Sr isotopes. The robustness of using $^{87}Sr/^{86}Sr$ to determine the origin of foods from young volcanic islands has been used successfully on Hawaiian coffee, where the lowest $^{87}Sr/^{86}Sr$ values are seen on the youngest islands and the mean isotopic Sr is ~0.7065 [43].

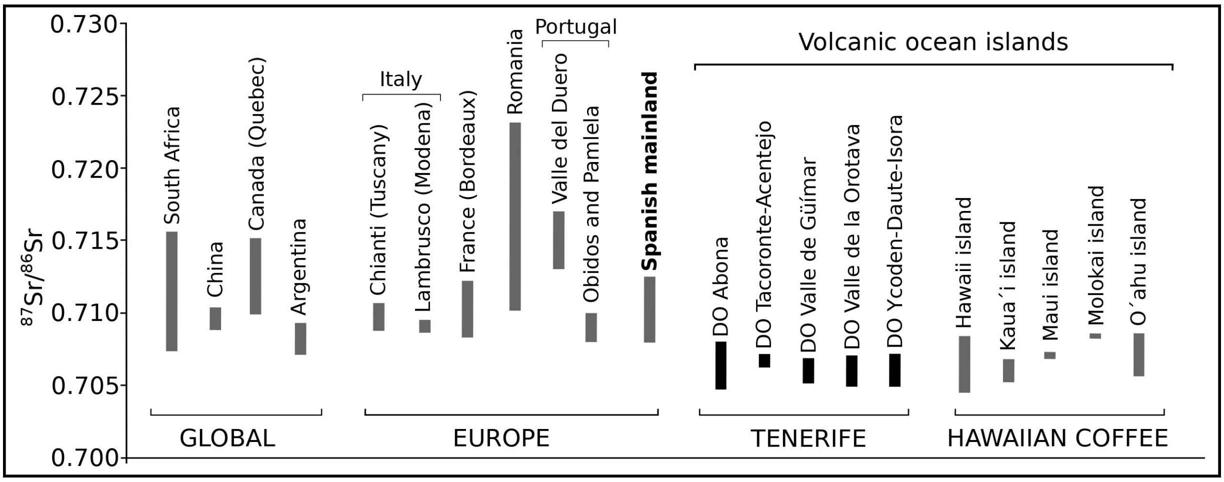

Figure 5. Sr isotopic signatures of Tenerife wine in a European and global context [11,13,44–48]. A comparison with another oceanic island setting (young, fresh rocks and soils) can be made by looking at the $^{87}Sr/^{86}Sr$ signature of Hawaiian coffee [43].

Tenerife is also distinct from other global wine-producing regions because of the relative difference between $^{87}Sr/^{86}Sr$ in the wine and that of the local rocks and substratum. $^{87}Sr/^{86}Sr$ has been repeatedly proven as an accurate tracer for wine provenance across Europe [17,40,41,49]. In other locations where vineyards are grown on volcanic terrain, $^{87}Sr/^{86}Sr$ from the local geology matches those from the wine because soils are fairly uniform and have not had time to develop differential weathering, etc. for bioavailable elements to differ spatially [15]. Tenerife is an exception to this general rule: wine samples are consistently $\geq$0.003 higher in $^{87}Sr/^{86}Sr$ than the island's basaltic and phonolitic bedrock compositions (Figure 6).

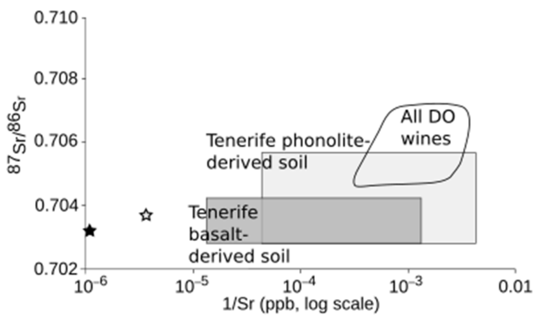

Figure 6. The relationship between Tenerife bedrocks, hypothetical soils derived from these and wines from the five Tenerife DO regions. Local basalt (black star; n = 110) and phonolite (white star; n = 37) averages from the GEOROC database [28], and Sr concentration range assigned by a typical derivation factor from the rock parent [23] (note the logarithmic scale, necessary to display both rocks and wines).

The demonstrated high accuracy, precision, and reproducibility of standards and ultra-low procedural blanks (Supplementary Materials Tables S1 and S2) rule out analytical bias. The elevation of $^{87}Sr/^{86}Sr$ in Tenerife DO wines above that of local bedrock therefore suggest that a small systematic radiogenic isotopic addition mechanism occurred. Determining how this offset between rocks and wine happens is significant for island viticulture and can serve as a reference case both for other agricultural products sold by origin and for other oceanic island territories seeking to qualify natural and anthropogenic influences. The following discussion outlines possible sources and addition mechanisms with reference to Tenerife's combination of geography, climate and geology.

4.3. Substratum Influence

All DO wines are elevated from the range of basaltic soil (bedrock) isotopic composition, and only around a quarter of wine samples overlap the higher end of the phonolite isotopic ratio range (Figure 6). As anticipated, the concentration of Sr in Tenerife wine is markedly lower than in these substratum rocks by several orders of magnitude due to differential mineral weathering processes and external inputs to a potential soil, and plants subsequently taking only bioavailable nutrients ('labile' [23]). However, as biologic processes do not fractionate Sr isotopes, the $^{87}Sr/^{86}Sr$ signatures in Tenerife wines indicate that there are other influences on the labile cations in the soil.

This non-geologic influence appears to be comprehensive across Tenerife, since the range of isotopic values measured in the wines follows that of the geology of their individual DOs. Felsic (generally phonolitic) deposits and soils display a larger range in isotopic composition compared with the basalts of Tenerife (Figure 6). Since a greater range of $^{87}Sr/^{86}Sr$ in wine is observed in the southern DO Abona and this is where most of the phonolite-derived soils are present, the geology clearly determines that range. The corollary is also true: basalt-dominated DO wines (e.g., Valle de la Orotava, Tacaronte-Acentejo) show more restricted isotopic ranges, as does the basaltic bedrock (Figures 4 and 6).

4.4. Natural Inputs of Sr

In order to fully characterise the provenance of Tenerife wine, the soil–vegetation system needs to be examined in terms of its primary and secondary inputs. The primary input (local bedrock) is inherently linked to wine (and other agricultural product) compositions [16,17,21,43], and the range of theoretical soil compositions can be constrained by using average substratum $^{87}Sr/^{86}Sr$ and Sr concentrations typical of soils in relation to rock (Table 4). Regular secondary inputs to island vineyards include rainfall, groundwater (especially where used for intensive irrigation), marine spray and atmospheric dust deposition.

Table 4. Natural inputs to the Tenerife viticulture system. Substratum rocks are 12–1200 times more enriched in Sr than their derivative soils [23]. These two endmembers constrain a soil composition based on the average basalt and phonolite compositions of Tenerife (basalt n = 110; phonolite n = 39 [28]). Average marine spray (n = 4), average local groundwater (n = 4) and rainfall samples (n = 2) collected locally and measured at the ITER TIMS facility, (1SD absolute given); southern Morocco Saharan dust composition (n = 8) [30].

Model Input	Sr concentration * (ppb)	$^{87}Sr/^{86}Sr$
Basalt "soil" average	769–76,921	0.703093
Phonolite "soil" average	232–23,172	0.703669
Marine spray	10,835	0.709175 (+/−0.00003)
Local groundwater (irrigation)	324	0.70372 (+/−0.00005)
Atmospheric deposition (rain)	21	0.710113 (+/−0.00002)
Southern Morocco Saharan dust (Calima)	90,000	0.72212

* estimated following [23].

- Rainfall

Rainfall around oceanic islands has the isotopic composition of local seawater because natural fractionation processes are negligible, and what miniscule amount may occur is corrected for in analysis [50]. Sr concentrations in rainwater are generally ~20 times lower than seawater through the process of evaporation [23]. In coastal areas in the north of Tenerife, precipitation is around 300 mm/year, rising to 800 mm/year at ~800 m elevation [51]. However, the south receives only around 200 mm/yr at higher elevations and almost nothing at the coast [52,53]: an island-scale rain shadow. Aside from rainfall, the isolated, steep landscape of Tenerife (rising to 3718 m a.s.l) in the Atlantic Ocean interrupts trade winds, causing a near-daily build-up of non-precipitating cloud on its slopes between 700 and 1500 m. This defines an atmospheric inversion layer between cool surface air and the warm overlying layer [53]. Despite the small geographic area of Tenerife (2034 km^2), these differences in precipitation and moisture availability are pronounced between DO regions. It is important to note that, in contrast to northern DOs that receive regular rainfall, agriculture in the south of Tenerife relies upon irrigation practices for healthy plant growth.

- Groundwater (irrigation)

Water is a valuable commodity on Tenerife, and agriculture is the main consumer [54]. Water for viticulture is mostly accessed from horizontal galleries and deep wells bored into the island aquifer, which is hosted predominantly in the older basaltic edifice (the coastal aquifer is distinct from the central island aquifer [55]. Groundwater is in isotopic equilibrium with its host rock, i.e., basalt (Table 4).

- Marine spray

Coastal areas of Tenerife are strongly impacted by north-easterly trade winds, which are directed and further strengthened on the southern coast of Tenerife due to channelling between the islands [56]. These winds often entrain marine aerosol, visible as a 'mist', which is blown onto the land. Marine spray has the same geochemical characteristics as local seawater (see Table 4).

- Atmospheric dust

Microscopic mineral dust derived from the arid belts of the Earth provide an important nutrient source to both the oceans and continents [57,58]. The African continent is one of the world's primary sources for remobilised mineral dust. The Sr isotopic signature of the dust reflects its origin, which in the case of the Canary Islands, is predominantly from the Sahara Desert of southern Morocco [30] (see Table 4). Discrete, intense dust events, termed locally as 'Calima' deposit, this dust, sometimes with rainfall [29]. Calima events affect the entire Island of Tenerife, and dust input has been quantified on nearby Gran Canaria from 79 g m^{-2} y^{-1} at coastal elevations to 17 g m^{-2} y^{-1} at ~1000 m a.m.s.l [59]. Dust events have occurred in the Canary Islands for ~80,000 years and are considered an integral part of Canary Island soils [60], with ~50% of the incoming dust stabilised into the soil profile [61].

4.5. Predicting Direct Effects of Natural Sr Inputs

Figure 7 displays ubiquitous, natural Sr inputs and the effects of direct mixing of these with a range of reasonable soil compositions calculated from local substratum compositions. Three inputs have elevated $^{87}Sr/^{86}Sr$ with respect to Tenerife wines. Irrigation (using groundwater) cannot raise isotopic Sr because the $^{87}Sr/^{86}Sr$ signature in groundwater is endemic to Tenerife geology (and therefore soils).

Southern Morocco Sahara dust is characterised by high Sr concentrations (high carbonate content [30]) and markedly elevated $^{87}Sr/^{86}Sr$. Island-wide deposition occurs numerous times a year and may either settle on plants (direct) or enter the soil system (indirect). As Sr concentration in Calima dust is so high, a direct influence is very unlikely: the effect of mixing even a tiny amount of dust pushes Sr concentrations to far higher values than those measured in Tenerife DO wines (Figure 7). However, once the dust has undergone weathering to produce labile Sr ions [50], the soil Sr concentration increases along with raising the isotopic signature of the bioavailable Sr. Although this contaminant source is not precluded, the limitation of labile ions immediately available from Calima dust after an event reduces the potential of short-term elevations of $^{87}Sr/^{86}Sr$ of the soils. Placing quantitative constraints upon the longer-term role of dust in the Tenerife soil system requires the study of island vineyard soil profiles and fossil soil carbonate horizons (in progress).

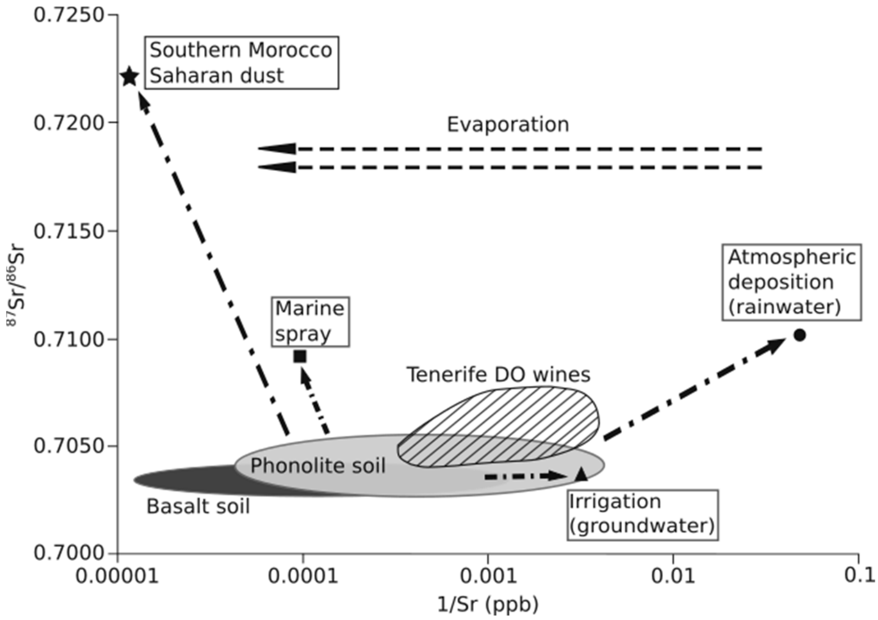

Figure 7. Simple direct-mixing relationships for common natural contaminants to the Tenerife soil system. Two ranges of hypothetical soil compositions are considered, based on dominant island basalt and phonolite (see Table 4). $^{87}Sr/^{86}Sr$ values and Sr concentrations typical of soils in relation to their parent rock [23]. Endmembers represent 100% of that contaminant. Southern Morocco Saharan dust compostion is modelled here because it is the dominant contributor to local Calima dust storm events [30]; marine spray composition is that of Atlantic seawater from around Tenerife; local groundwater is considered as proxy for irrigation practices; and atmospheric deposition (rainfall) from a heavy rain event gives the composition of matter scrubbed out of the atmosphere and added to the soil system (which may contain dust and pollution particulates as well as the freshwater rain [62]). Intense evaporation in a desert environment (e.g., in the south of Tenerife) causes an increase in the Sr concentration without affecting the $^{87}Sr/^{86}Sr$ composition [63]. Pollution contribution to rainfall similarly increases Sr concentrations [62].

Water-based inputs have the potential to immediately affect the soil–vegetation system. Atmospheric deposition can provide up to 65–75% of Sr flux [23,64]. Marine spray is a constant potential source of Sr and is driven inland (particularly in the south) by winds around Tenerife. Given its seawater Sr isotopic signature, settled spray could raise the isotopic signature of the soil system or the $^{87}Sr/^{86}Sr$ of grapes entering the wine making process. Modelling direct-mixing indicates that the high Sr concentration of seawater makes this contaminant unlikely because the unfeasibly large volume of seawater (80–90%) required to elevate DO isotopic signatures would also increase Sr concentrations above those in wines (Figure 7). Rainfall (which includes both water and atmospheric particulate matter) at elevated $^{87}Sr/^{86}Sr$ with respect to Tenerife wines has very low initial Sr concentrations (Table 4). Rainfall rapidly dilutes the Sr concentration of soil during percolation as well as diluting Sr in local volcanically hosted groundwaters without completely overprinting the local isotopic signatures [50,65]. Modelling indicates the basaltic/phonolitic soil–vegetation system requires ~0.5–4% of rainfall to elevate $^{87}Sr/^{86}Sr$ by ~0.002 above soils whilst depressing Sr concentrations to the ranges measured in Tenerife DO wines.

In the south of Tenerife, at low elevations, evaporation may play an important role in vineyards that are dominantly irrigated. Given that irrigation does not affect the isotopic ratio derived from bedrock, the evaporation of groundwater serves only to increase the Sr concentrations.

4.6. Tracing Variable Influences

The influence of these four secondary inputs to the Tenerife terroir can vary widely over the micro-climates. Projecting the wine data by DO helps to understand which, and where, those influences are most important. Wines from the northern DOs of Tacoronte-Acentejo and Valle de la Orotava form more elongate fields of variable (and low) Sr concentrations within a restricted range of $^{87}Sr/^{86}Sr$ (Figures 3 and 4). This is consistent with the higher annual rainfall received in that region onto dominantly basaltic soils. The southern DOs of Abona and Valle de Güímar, which are subjected to strong trade winds and markedly less rainfall, have higher average Sr concentrations and more variable $^{87}Sr/^{86}Sr$ in their wines. This likely reflects the greater range of $^{87}Sr/^{86}Sr$ in dominantly phonolitic soils, together with stronger evaporative influences buffering Sr at slightly higher concentrations than the northern DOs (Figure 3).

The western Ycodon-Daute-Isora DO, which spans a large area of both northern and western slopes, also shows an elongate isotopic field with two groups of samples: one at similar Sr concentrations to other DO samples and one with lower Sr concentrations (Figure 4). The geographic and orographic expanse of this region makes it harder to discern a dominant influence on the DO wine signature. The steep terrain often means that the vineyards are at altitude and frequently in orographic cloud. They are subject to more water input by condensation than lower altitude vineyards, affecting the bioavailability of elemental Sr in the soil [50,66].

Of the 81 Tenerife samples analysed (five regional DOs plus DO Tenerife and guachinches; Supplementary Material Table S4), 90% fall in the range 0.7045–0.7072, with DOs forming elongate fields in elemental and isotopic space up to this "isotopic Tenerife wine maximum" (Figure 8, Supplementary Material Table S5). Nine samples fall outside this range: three from DO Abona, three from DO Tenerife and three from guachinche restaurants. These samples have $^{87}Sr/^{86}Sr$ signatures similar to wine samples from the Spanish mainland at >0.708 (Figure 8). This observation is a concern for wines under registered DO labels in particular.

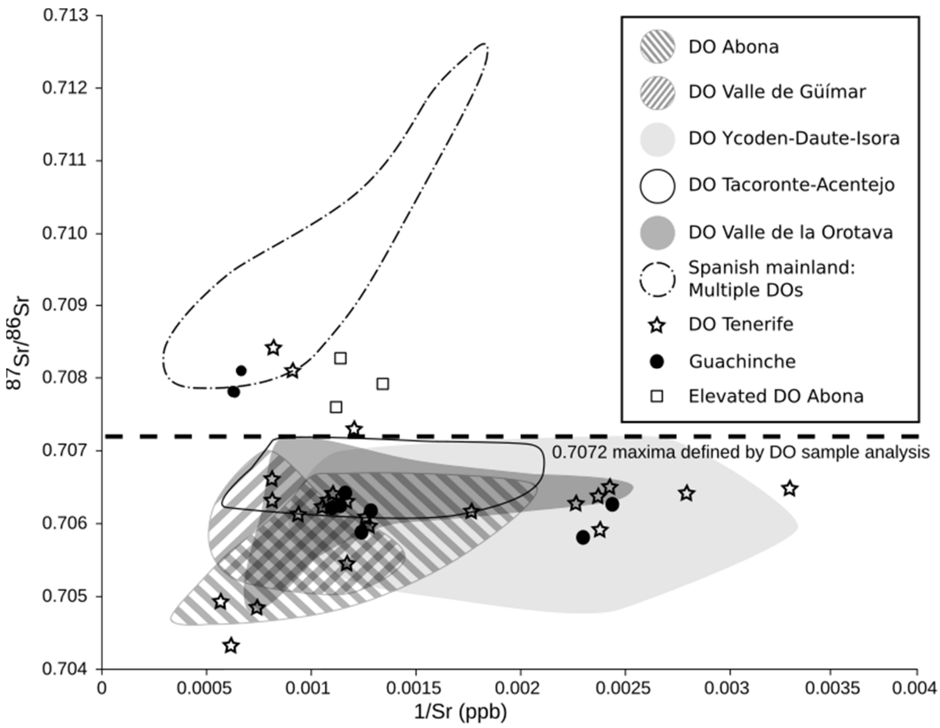

Figure 8. DO fields from Figure 4, with samples from DO Tenerife, guachinche restaurants and Spanish mainland samples (Supplementary Materials Table S4). Ninety percent of the DO registered Tenerife samples define a 0.7072 maxima for $^{87}Sr/^{86}Sr$ (also evaluated as a rank-order plot in Supplementary Materials Table S5, where a sharp inflection can be seen above this maxima).

Since the data do not support a ubiquitous anthropogenic source of radiogenic Sr, it is possible that the outliers imply that some wine-mixing practices have occurred in a limited number of tested samples. Tenerife-labelled wines with outlying $^{87}Sr/^{86}Sr$ signatures and Sr concentrations similar to Spanish mainland wine samples (Figure 8) support a hypothesis of bulk product being purchased and either mixed with, or simply rebadged as, a Canarian product.

5. Conclusions

Geochemical and isotopic provenance is becoming an indispensable tool to combat the multi-million Euro problem of fraud in the agricultural industry. However, this normally robust geographic tracer can be subjected to influences that subtly raise the isotopic Sr ratio of the terroir. In Tenerife, atmospheric precipitation directly effects the $^{87}Sr/^{86}Sr$ of wines in the northern DOs of Tacoronte-Acentajo and La Orotava, where rainfall is higher. Southern DO regions may be affected by atmospheric moisture at the temperature inversion layer (regular cloud layer), but an evaporative influence likely buffers Sr concentrations to lower levels in these drier DOs. The low intial $^{87}Sr/^{86}Sr$ imparted by the ocean island basaltic bedrocks allow these atmospheric precipitation pathways to be visible despite wine enhancement techniques. Determining the importance of indirect processes, such as dissolution/re-precipitation of settled atmospheric mineral dust within the Tenerife soil system, will define the natural plausible range and improve confidence in DO products. A database for "fingerprinting" the full, and complex, oenological system including bedrock and other natural sources of Sr, soil, the vines and the finished wine product would be a distinct advantage.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/beverages8010009/s1, Supplementary Material Figure S1: Cross analysis of wine samples by TIMS at University of Aveiro and ITER; Supplementary Material Table S1: Measurements of international Sr isotope standard NIST987 at the ITER TIMS facility; Supplementary Material Table S2: ITER Clean laboratory blank concentrations; Supplementary Material Table S3: University of Aveiro (Portugal) Sr purification methodology; Supplementary Material Table S4: Results: $^{87}Sr/^{86}Sr$ and Sr concentrations, this study; Supplementary Material Table S5: $^{87}Sr/^{86}Sr$ of Tenerife wines in rank order.

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