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Strontium isotope characterization of wines from Quebec, Canada

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ABSTRACT

The $^{87}Sr/^{86}Sr$ isotope ratios were measured on grape, wine and soil samples collected in 13 commercial vineyards located in three major wine producing areas of Quebec (Canada). The soils yield Sr isotope ratios that are intimately related to the local geology and unambiguously discriminate the different producing areas. A strong relationship exists between the $^{87}Sr/^{86}Sr$ isotope ratios of the wine and the grapes. This suggests that the vinification process does not alter the overall Sr budget. Although the Sr isotope ratios of the grapes do not show a strong correlation with the bulk Sr isotope composition of the soil, they do correlate strongly with the Sr isotope composition contained in the labile fraction of the soil. This indicates that the labile fraction of the soil represents the Sr reservoir available to the plant during its growth. This study demonstrates that the Sr isotope approach can be used as a viable tool in forensic science for investigating the provenance of commercial wines.

1. Introduction

The certification of food products, their authenticity and origins has become a growing priority amongst consumers and producers. This is especially true for wines whose commercial value is associated with their region of production. The strong association of wine and terroir led to the creation of protected geographic appellations in major wine producing areas worldwide. In Quebec (Canada), the wine industry has been developing rapidly over the last decade (Pedneault, Dorais, & Angers, 2013). Current wine production regulations allow for the addition of up to 15% of grapes from outside of the production region. However, in order to protect and increase the value of locally produced wines and strengthen the local market, the Quebec government has been working on the application of a Protected Geographical Appellation label which will require 100% of the grapes to be derived from the production region (appellation Quebec law c. A-20.03, r.2). The differentiation of the different Quebec wine terroirs as well as terroirs around the globe necessitates the development and implementation of forensic tools to link wines to their corresponding terroir. A number of different analytical techniques have been evaluated for the purpose of wine authentication such as major and trace elements (Castineira, Brandt, Von Bohlen, & Jakubowski, 2001; Galani-Nikolakaki, Kallithrakas-Kontos, & Katsanos, 2002; Lara, Cerutti, Salonia, Olsina, & Martinez, 2005), pH-values, radioactivity (Hubert, Pravikoff, & Gaye, 2015), stable isotopes (Allen, Lacey, & Boyd, 1994), infrared spectroscopy and DNA markers (Siret, Boursiquot, Merle, Cabanis, & This, 2000) and Sr isotopes. Strontium isotopes reflect the local geological conditions of the wine terroir and may therefore be linked to the origin of the grape used for wine production. The Sr isotope composition of terrestrial vegetation is dominated by the Sr isotope ratio of labile Sr in the soil, which is influenced by the age and composition of the bedrock and till (Banner, 2004; Faure, 1986; White, 2013), soil water properties and atmospheric inputs (Barbaste, Robinson, Guilfoyle, Medina, & Lobinski, 2002; Stewart, Capo, & Chadwick, 1998). Biological processes of the plant do not fractionate radiogenic Sr isotope ratios (Capo, Stewart, & Chadwick, 1998). An investigation into the Sr isotope compositions of labile Sr in the soil and in the plants growing in a defined geographic area found differences of up to 0.5% in the corresponding $^{87}Sr/^{86}Sr$, which were interpreted to reflect variations in the amounts of dust, differential weathering of the underlying rocks and the proportion of soil constituents contributing to the overall Sr budget in the soil (Sillen, Hall, Richardson, & Armstrong, 1998).

The correlation of the $^{87}Sr/^{86}Sr$ isotope ratios between soil and plant, make it an interesting tool for tracing the provenance of agricultural produce such as grapes and wine (Åberg, 1995). This method is based on the principle that plants absorb labile elements in the same isotopic proportions that occur in the soil (Comerford, 2005; Johnston & Goulding, 1990) and that Sr isotopes can be used

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as a proxy for labile base cations in tracing the source of soils nutrients in the soil-plant system (Bailey, Hornbeck, Driscoll, & Gaudette, 1996; Drouet, Herbauts, Gruber, & Demaiffe, 2005). Several studies have demonstrated that the $^{87}Sr/^{86}Sr$ ratio is an optimal geographic footprint for food and animal products because Sr is actively involved in the metabolism of the plants but undergoes little fractionation during the various biological processes involved in plant development (Asfaha et al., 2011; Blum, Taliaferro, Weisse, & Holmes, 2000; Camin et al., 2007, 2009; Capo et al., 1998; Crittenden et al., 2007; Fortunato et al., 2004; Ghidini et al., 2006; Kelly, Heaton, & Hoogewerff, 2005; Luykx & Van Ruth, 2008; Price, Burton, & Bentley, 2002; Schellenberg et al., 2010; Stewart et al., 1998; Voerkelius et al., 2010). Variations in the $^{87}Sr/^{86}Sr$ isotope ratios in wine have been used to differentiate the geographic origin of wines in wine-producing countries such as Italy (Boari et al., 2008; Durante et al., 2015; Marchionni et al., 2013; Petrini et al., 2015), Romania (Dehelean & Voica, 2011), Germany (Hocq & Dubé, 1994; Wolff-Boenisch, Todt, Raczek, Horn, & Hölzl, 1998), South Africa (Vorster, Greeff, & Coetzee, 2010), Argentina (Di Paola-Naranjo et al., 2011) and France (Barbaste et al., 2002; Lurton, Lancelot, Herreiras, & Verdoux, 1999).

This study provides new Sr isotope data for soils, grapes and wine derived from 13 vineyards from different regions of Quebec that i) demonstrate the continuity of the isotope composition from the soil, through the grapes to the wine, and ii) provide constraints for determining the geographic origin of locally produced wines.

2. Materials and methods

2.1. Sampling strategy

Soil (13 samples), grape (16 samples) and wine (17 samples) were derived from 13 vineyards located in different wine producing areas of the Quebec province (Canada) and are listed in Table 1. The geographic areas selected for the study are the Estrie, the Montérégie and the Quebec City regions, including the Island of Orleans (Fig. 1). These regions are underlain by distinct geological formations with well-defined ages: the St-Lawrence Platform (upper and middle Ordovician) and the Appalachian Orogeny (Cambrian and lower Ordovician). The St-Lawrence Platform within the study area consists predominantly of non-deformed Cambrian-Devonian sedimentary rocks that overlay Precambrian metamorphic rocks of the Grenville Province (Hocq & Dubé, 1994; Tremblay, Hébert, & Bergeron, 1989; Tremblay & Bourque, 1991). The Appalachian province consists of deformed Cambrian and Paleozoic volcanic and sedimentary units that were thrust over the St-Lawrence Platform and Grenville Province along the Logan Fault. The sampled vineyards in the Estrie and Quebec City area are underlain by rocks of the Appalachian province that consist of 2 distinct lithologies (Gauthier et al., 1990): i) Cambrian-Ordovician sedimentary and volcanic rocks that were formed in an ocean basin and subsequently, folded, faulted and stacked during the Taconic orogeny; and ii) less distorted Silurian-Devonian sedimentary and volcanic rocks that formed in a shallower basin and were deformed during the Acadian orogeny. The vineyards of the Montérégie region are largely underlain by sedimentary rocks of the St-Lawrence Platform and these rocks are mostly sandstone, dolomite, limestone and shale (Castonguay, Dietrich, Morin, & Laliberté, 2001). Large variations in the $^{87}Sr/^{86}Sr$ ratios were already reported (e.g. McNutt, Frape, & Dollar, 1987; Roulleau & Stevenson, 2013) from 0.703 to values more radiogenic than 0.711 (i.e. $^{87}Sr/^{86}Sr > 0.711$) related to the broad range of lithologies and geological ages found within the study area.

For this study, different varieties of red grapes were collected: Frontenac, Maréchal Foch, Marquette, Sabrevois and St. Croix. These varieties are grown in the Quebec province because they can tolerate cold winters (Slegers, Angers, Ouellet, Truchon, & Pedneault, 2015). Frontenac (*V. riparia 89* × French grape *Landot 4511*) and Marquette (*Mn 1094* × *Ravat 262*) are hybrid cultivars

Table 1
$^{87}Sr/^{86}Sr$ ratios for wine, grape, bulk soil and labile soil fractions from selected Quebec vineyards.

Vineyards	Grape variety	Geology	Wine		Grape		Bulk soil		Labile soil	
			$^{87}Sr/^{86}Sr$	2 σ	$^{87}Sr/^{86}Sr$	2 σ	$^{87}Sr/^{86}Sr$	2 σ	$^{87}Sr/^{86}Sr$	2 σ
(1) Côte de Vaudreuil	Sabrevois	St-Lawrence platform	0.71021	0.00001	0.70945	0.00002	*nd*		*nd*	*nd*
(2) Domaine de Lavoie	Sainte Croix	St-Lawrence platform	0.71078	0.00001	0.71046	0.00002	0.71267	0.00002	0.71211	0.00002
	Maréchal Foch		0.70988	0.00001	0.70987	0.00003	0.71310	0.00002	0.70986	0.00001
(3) Les Artisans du terroir	Marquette	St-Lawrence platform	0.71013	0.00001	0.70994	0.00001	0.71578	0.00001	0.70979	0.00002
(4) Les Petits Cailloux	Sainte Croix	St-Lawrence platform	0.71138	0.00001	0.71070	0.00001	0.71203	0.00004	*nd*	*nd*
(5) Viticulture A et M	Marquette	St-Lawrence platform	0.71018	0.00001	0.71026	0.00002	0.71538	0.00002	0.71036	0.00002
(6) Côte du Limousin	Sabrevois	Appalachian platform	0.71306	0.00002	0.71330	0.00002	0.71964	0.00002	0.71335	0.00002
(7) Les Bromes	Maréchal Foch	Appalachian platform	0.71108	0.00001	0.71093	0.00016	0.71571	0.00003	0.71174	0.00003
(8) La Mission	Sabrevois	Appalachian platform	0.71437	0.00003	0.71482	0.00002	0.72345	0.00002	0.71363	0.00007
(9) La Bauge	Marquette	Appalachian platform	0.71072	0.00002	0.71065	0.00002	0.71746	0.00002	*nd*	*nd*
(10) L'Ange Gardien	Maréchal Foch	St-Lawrence platform	0.71018	0.00002	0.70954	0.00003	0.72186	0.00002	0.71012	0.00002
(11) Sainte-Petronille	Sainte Croix	Appalachian platform	0.71395	0.00002	0.71257	0.00115	0.73418	0.00002	*nd*	*nd*
	Frontenac		0.71305	0.00002	0.71253	0.00002	0.73230	0.00001	*nd*	*nd*
(12) Isle de Bacchus	Marquette	Appalachian platform	0.71513	0.00002	0.71522	0.00001	0.72666	0.00001	0.71546	0.00002
	Frontenac		0.71351	0.00002	0.71373	0.00003	*nd*	*nd*	*nd*	*nd*
	Maréchal Foch		0.71546	0.00001	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*
(13) Domaine de la source à Marguerite	Marquette	Appalachian platform	0.71206	0.00001	0.71206	0.00002	*nd*	*nd*	*nd*	*nd*

nd: not determined.