Rare Earth Elements Distribution in Grape Berries

Distribution d'éléments chimiques rares dans les baies de raisin

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Abstract

Rare Earth Elements (REEs) include 15 lanthanides, yttrium and scandium. Their occurrence in soil and plants seems to be closely tied to the geological composition of the underlying mother rock, to the physical and chemical properties of the soil and to the specific ability of the plant to take up and accumulate these microelements. To date knowledge regarding the composition and distribution of trace elements in *Vitis vinifera* has been lacking or is inadequate. The aim of this research was to study REEs distribution in Chardonnay berries harvested at ripeness in 2006 in Trentino (north-eastern Italy).

After washing and microwave acid digestion, both the total REEs content in the berries and the REEs distribution within the skin, seeds and flesh were quantified. Analysis of 13 elements (yttrium, Y; lanthanum, La; cerium, Ce; praseodymium, Pr; neodymium, Nd; samarium, Sm; europium, Eu; gadolinium, Gd; dysprosium, Dy; holmium, Ho; erbium Er; thulium, Tm; ytterbium, Yb) was carried out with an inductively coupled plasma mass spectrometer.

The total REEs content measured in berries was 2.079 μg/kg of fresh weight. The order in terms of percentage content within the berry was skin > flesh > seeds ($p<0.05$) for Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho and Er. For Tm and Yb there were no significant differences between the skin and flesh. Eu showed a significantly different distribution pattern.

Keywords: Rare Earth Elements, berry, seed, skin, ICP-MS

Introduction

Rare Earth Elements (REEs) are a group of elements with very homogeneous characteristics including 15 lanthanides, plus yttrium and scandium, which have similar properties. In general REEs occur as a trivalent cation with exceptions concerning in particular cerium and europium, which could also be present as Ce^{+4} and Eu^{+2}.

REEs occurrence in soil and plants seems to be closely tied to the geological composition of the underlying mother rock, to the physical and chemical properties of the soil and to the specific ability of the plant to take up and accumulate these microelements (Kabata-Pendias, 2001). These characteristics make REEs, at least apparently, an ideal group of elements for tracing agricultural and food products (such as grapes) that have not already undergone technological treatments modifying the original content (Larcher and Nicolini, 2008).

Much research seems to indicate that low amounts of REEs applied to seeds or crops may promote the growth and productivity of various species (Tyler, 2004; Hu et al., 2004). REEs fertilisation in agriculture is widely practised in China but their physiological functions, and ecological and toxicological impact are still not known in detail. REEs, Lanthanium in particular, have characteristics biologically similar to calcium, and also seem to be beneficial for photosynthesis (Brown et al., 1990; Hu et al., 2004).

The content of trace elements in different tissues in *Vitis vinifera* has received little attention, with some exceptions mainly concerning toxic metals in industrialised/polluted areas (Pertoldi Marletta et al., 1989; Angelova et al., 2001) or other heavy metals in grapes (Orescanin et al., 2003). Recently, Oddone et al. (2006), studied the REEs content and pattern in soil, grapes and wine.

The concentration of REEs in plants is very variable, ranging from below 1 ppb to above 15000 ppb of dry weight; generally being more abundant in woody plants than in vegetables (Kabata-Pendias, 2001) and in decreasing amounts in root, leaf, stem, flower, fruit and seeds (Sun et al., 1994; Hu et al., 2004). The aim of this research was to study REEs distribution in Chardonnay berries (divided into skin, seeds and flesh) at ripeness: this knowledge would also be important for predicting the transfer of elements from grapes to wine during vinification.

Material and methods

The vineyard, located in S. Michele all'Adige, Trentino (north-eastern Italy, 240 m a.s.l.), with WSW exposure, no manure treatments and on a grass-covered plot, was divided into 4 parcels of 54 grapevines each, managed with Guyot trellising (1.6 x 1 m). The grapes belonged to the Chardonnay variety, clone 95, grafted onto rootstock 3309 (*V. riparia x V. rupestris*). Information about the host soil is given in Bertoldi et al., 2008.
In 2006, from 2 weeks before until 2 weeks after technological harvesting (from 29 to 57 days after veraison), 200 berries were picked from 20 bunches for each harvest date and parcel.
All the samples were washed with a 1% ultrapure nitric acid solution. Each sample was divided into 2 parts: 100 berries, used for quantification of the total REE content , were immediately homogenised using Ultra-turrax (IKA, Germany) whereas 2 portions were obtained from the other 100 berries: skin and seeds. In detail, before homogenisation, the berries were peeled and the skin was rasped to remove the flesh residue and then dried with clean paper. The seeds were cleaned, dried and added together with an equal weight of ultrapure water. The samples were acid digested using a microwave system (MARS EXPRESS, CEM, USA) equipped with 75 ml PTFE vessels. Four millilitres of ultrapure HNO_3 (96.5%, Merck, Germany), 5 ml of ultrapure water and 1 ml of internal standard solution (Rhenium, 800 μg/L) were added to 1.5 g of seeds or skin or to 2.5 g of berries. The digestion conditions are specified in the table below:

ramp (min)	holding time (min)	Temperature (°C)
8	5	100
10	5	150
12	10	210

REEs analysis was performed using an inductively coupled plasma mass spectrometer (ICP-MS, 7500ce, Agilent Technologies, Japan) equipped with an autosampler ASX-520 (Cetac Technologies, USA), a MicroMist nebulizer, a quartz Fassel-type torch, Ni-cones and a collision/reaction cell used in helium mode for the quantification of europium to remove polyatomic interferences. Thirteen REEs were quantified using the following isotopes: yttrium (Y, 89), lanthanum (La, 139), cerium (Ce, 140), praseodymium (Pr, 141), neodymium (Nd, 143), samarium (Sm, 147), europium (Eu, 151), gadolinium (Gd, 160), dysprosium (Dy, 163), holmium (Ho, 165), erbium (Er, 167), thulium (Tm, 169), ytterbium (Yb, 171). A solution of Rhodium (3 mg/L) was used as the on-line internal standard.
The REEs content in flesh was calculated as the difference between the level in the whole berry and in the skin plus seeds. Statistical analysis (HSD Tukey test) was performed with STATISTICA 6.1 for Windows (StatSoft Italia srl, Italy).
The basic composition of the juices was analysed weekly using a FT-IR (Foss Italia, Italy).

Results and discussion

All the grapes sampled were characterised by a high level of ripeness (Table 1).

days after veraison	°Brix	pH	Total Acidity (g/L artaric acid)	Tartaric acid / Malic acid
29	21.79	3.44	6.77	3.65
36	23.15	3.43	6.53	4.28
43	24.27	3.60	5.86	5.82
50	23.71	3.54	5.50	5.84
57	24.50	3.69	5.34	11.11

Table 1 Oenological parameters analysed in juices. The values given are the mean for 4 parcels.

As no notable differences in total content and distribution within the berry were observed for the different harvest dates, we will discuss the data without distinguishing between the sampling time.
The total content (median value, n=20; µg/kg berries, fresh weight) of the analysed elements was as follows: Y (0.0989 µg/kg), La (0.3692 µg/kg), Ce (0.8693 µg/kg), Pr (0.0933 µg/kg), Nd (0.4155 µg/kg), Sm (0.068 µg/kg), Eu (0.0416 µg/kg), Gd (0.0526 µg/kg), Dy (0.0288 µg/kg), Ho (0.0062 µg/kg), Er (0.0148 µg/kg), Tm (0.0047 µg/kg), Yb (0.0162 µg/kg). The distribution of values for each element is shown in Fig. 1. Generally, as reported in literature (Kabata-Pendias, 2001) the content of REEs with a lower atomic number was higher: in our samples La, Ce e Nd made up about 80% of the total REEs. A similar percentage content is also reported in must (Gomez et al., 2004) but the amounts (in absolute values) are lower than those showed in Oddone et al. (2006) for grapes. Moreover, the element with an even atomic number was more abundant than the next with an odd atomic number as stated in the Oddon-Harkins rule (Kabata-Pendias, 2001).

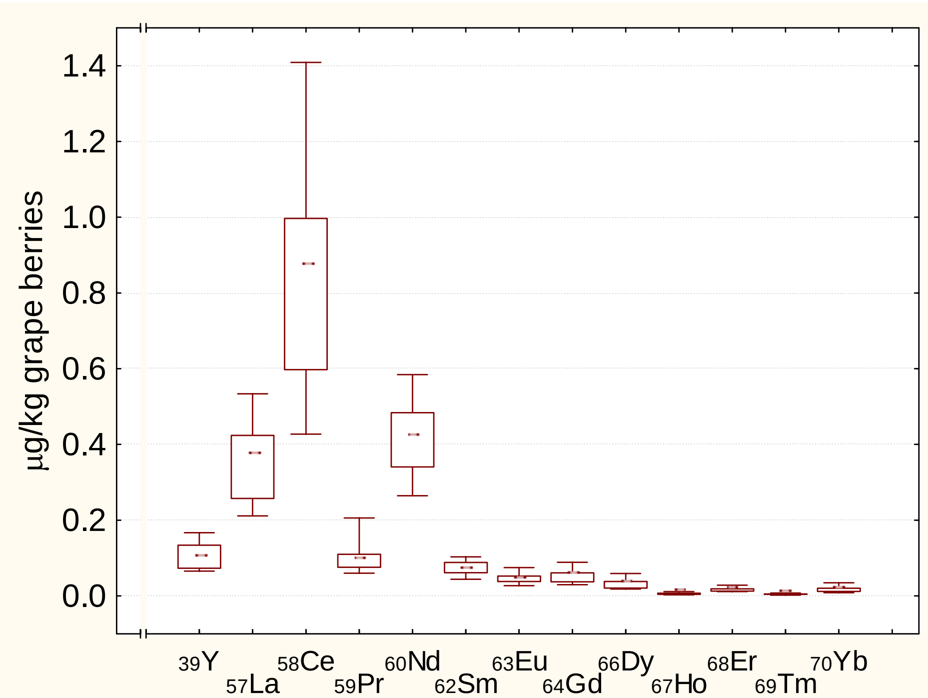

Figure 1 REEs content (expressed in µg/kg of fresh weight) in the berry. The elements are placed in order according to increasing atomic number.

As shown in Fig. 2, the order in terms of percentage content within the berry was skin (mean value 60%) > flesh (37%) > seeds (3%) for Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho and Er (significance at 5% minimum). This particular distribution could be explained by the cytolocalization of REEs and the role of these elements in the photosynthetic tissue (Hong et al., 1999, Hu et al., 2004). The percentage

content of Tm and Yb was not statistically different for skin and flesh and equal to 47-48%, the seeds containing the residual 4-6%.
The distribution pattern of Eu was different from that of the other REEs: the seeds showed the highest percentage content (45%) followed by skin (32%) and flesh (24%).

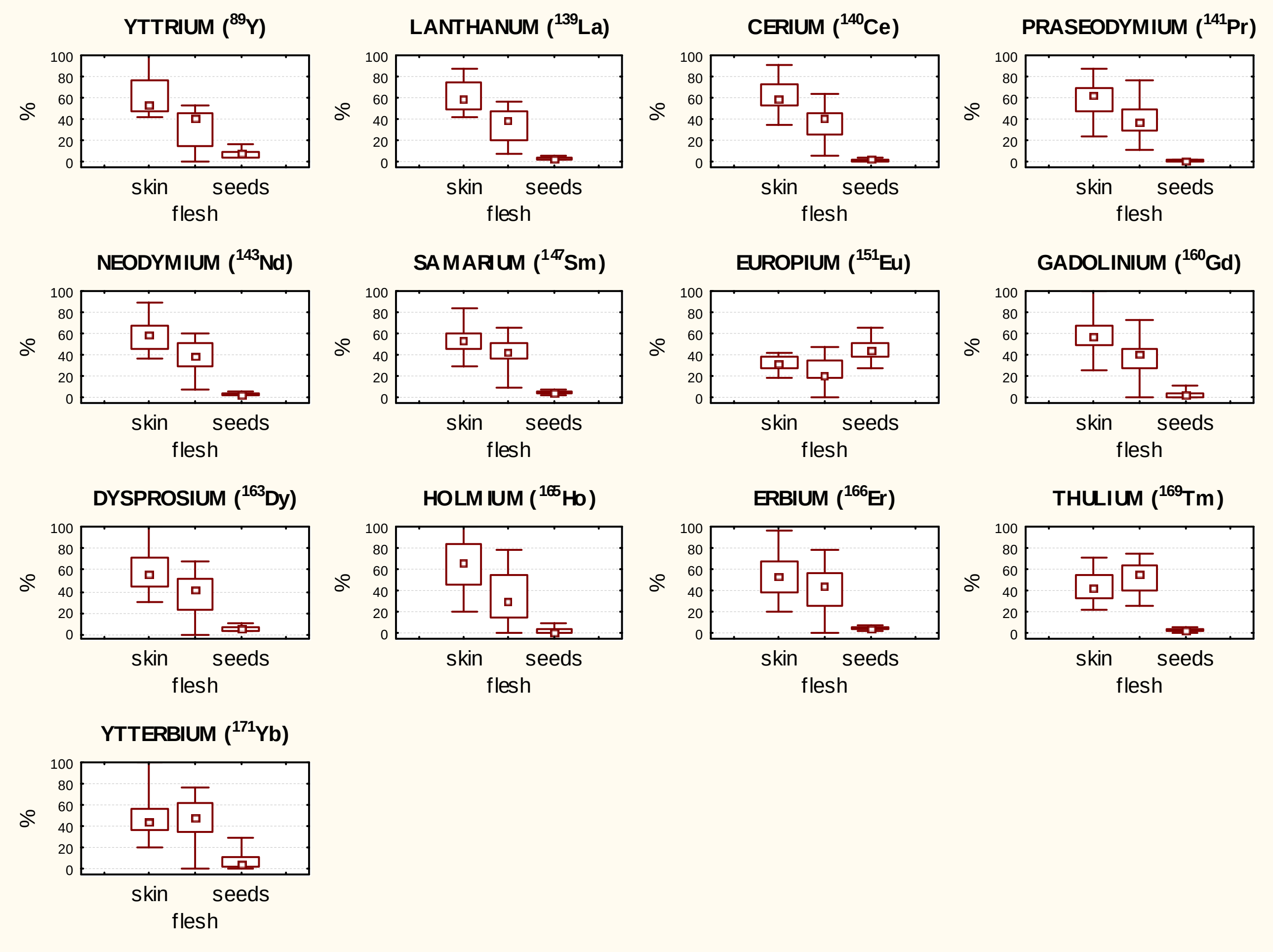

Figure 2 Distribution of different REEs in skin, flesh and seeds. Percentage expressed with respect to fresh weight. Caption as in Fig. 1.

Conclusion

The paper shows the first results obtained with a PhD project on micro, trace and ultra trace element composition and the distribution pattern in soil and in different organs of *Vitis vinifera*. It has increased knowledge about this subject, with the scope of contributing towards geographic traceability studies of grapes. Further research is necessary to confirm the distribution observed over several years and with different soils.

Aknowledgements

The authors wish to thank Cinzia Dorigatti for her support during sampling. This work was realised within the context of a PhD project on Viticulture, Oenology and Marketing at the University of Padova.

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