

# VOLCANIC SOILS COMPOSITION IMPACT ON THE MAJOR MINERAL ELEMENTS CONTENT OF GRAPES AND WINES

## INFLUENCE DES SOLS VOLCANIQUES SUR LA TENEUR EN ÉLÉMENTS MINÉRAUX MAJEURS DES RAISINS ET DES VINS

Maria T. RIBEIRO De LIMA<sup>1,\*</sup>, Marie T. CABANIS<sup>2</sup>, Geneviève CASSANA<sup>3</sup>,  
Lurdes Matos<sup>1</sup>, J. PINHEIRO<sup>1</sup>, J.-Cl. CABANIS<sup>2</sup> and A. BLAISE<sup>2</sup>

1 : Departamento de Ciências Agrárias, Universidade dos Açores,  
9700 Angra do Heroísmo, Terceira, Açores

2 : Centre de formation et de recherche en œnologie, Faculté de Pharmacie,  
15 avenue Charles Flahault, B.P. 14.491, 34093 Montpellier cedex 5, France

3 : Laboratoire de physique industrielle et traitement de l'information, Faculté de Pharmacie,  
15 avenue Charles Flahault, B.P. 14.491, 34093 Montpellier cedex 5, France

**Abstract** : The analysis of potassium, sodium, calcium and magnesium was carried out in soils, grapes and wines of wine regions of the Azores in order to obtain a mineral profile of the principal major elements. It would be of interest to achieve a profile of these minerals, according to the climate, to the position of the Islands and to their volcanic soils. Determinations were carried out by atomic absorption in flame. A statistical analysis of the findings was performed. This study establishes the diversity of wine regions in the Azores. As a whole, the amounts in the wines are in the european average.

**Résumé** : La recherche du potassium, sodium, calcium et magnésium a été effectuée dans des sols, raisins et vins des régions viticoles des Açores afin de réaliser un profil minéral moyen des principaux éléments majeurs. L'intérêt de définir un tel profil vient surtout du fait du climat particulier de ces îles, de leur position au milieu de l'Océan et de leur sol volcanique. Les mesures ont été faites par spectrophotométrie d'absorption atomique en flamme directement sur le vin et après minéralisation, par la technique du micro-ondes, sur les raisins et les sols. Les échantillons pour l'étude des sols ont été prélevés à deux profondeurs : la première à environ vingt centimètres et la deuxième à environ quarante centimètres. Pour chaque prélèvement de sol, la quantité totale de chacun des métaux ainsi que leur quantité directement assimilable par la vigne ont été mesurées. L'évaluation statistique des résultats par analyse de variance a permis de montrer que, pour les quatre éléments minéraux étudiés, les sols ont des teneurs distinctes d'une région à l'autre. La région de Graciosa est la plus riche en potassium. La région de Pico est la plus riche en sodium et en magnésium, enfin la région de Biscoitos est la plus riche en calcium. Pour les raisins les teneurs ne suivent pas toujours celles des sols ; en effet il n'existe pas de corrélation directe mais le sol n'est pas le seul facteur influant sur le raisin. L'environnement, le climat et la culture de la vigne ainsi que les traitements ont des effets importants sur la teneur des raisins. Dans les vins les quantités de sodium et de calcium sont différentes d'une région à l'autre mais sont semblables pour le potassium et le magnésium. Le sodium dit excédentaire reste à surveiller, l'Office International de la Vigne et du Vin ayant proposé une limite de soixante milligrammes par litre. La teneur en calcium est légèrement élevée mais rappelle les quantités trouvées au Portugal continental. Dans l'ensemble les quantités mesurées dans les vins sont celles des moyennes européennes. Cette étude a permis de bien mettre en évidence la diversité des régions viticoles des Açores.

**Key words** : major elements, wine, grapes, soil, atomic absorption

**Mots clés** : éléments majeurs, vin, raisin, sol, absorption atomique

### INTRODUCTION

Different regions original by climate, soil and grape varieties allow the production in Portugal of wines of character which would be worth knowing more thoroughly, particularly as regards the wine regions of the Azores.

Chemical analysis is one means of acquiring knowledge, but the number of compounds of such a matrix are so numerous that a choice must be made to reach the desired goal, namely the profile of the wines from these regions. The mineral substances of grapes, then of wines, result from the soils on which vines have been planted. They contribute to reflect what is called terroir, which gives wines their characteristic. That is why

our study was carried out on these elements. The latter being numerous, we have selected the mineral elements called major elements, i.e. those whose concentrations in wines reach ten mg/l to or more g/l. These elements are significant because they vary with the nature of the soils, the methods of cultivation, the rootstocks, the varieties and the weather conditions. Moreover, they vary according to the different technologies applied for the transformation of grapes into wine, then the ageing methods once the wine is finished.

Our study will be limited to the study of potassium, calcium and magnesium. Our choice was made in relation to the importance of each element. Indeed, potassium salts constitute an essential element of plant life. The vine is a species which absorbs it in great quantities, consequently potassium becomes the major cation in grapes. Volcanic soils constituting the majority of the soils in the Azores, contain a large quantity of alunite (aluminium and potassium sulphate), as well as oceanic sediments rich in iron and potassium silico-aluminate (PASCAL, 1963). Sodium does not play such an essential role to the plant as potassium. However, on average, it accounts for 30.6 % of the salts dissolved in the oceans. On the contrary, as it plays a

significant role in animal life, the Office International de la Vigne et du Vin has given a limit of «excess» sodium for wines, namely the sodium found outside the combination NaCl, which accounts for 60 mg/l. Magnesium is present in chlorophyll, in concentrations of up to 2.7 % in the form of an organo-metallic combination. In plants, it plays a part in the assimilation of the CO<sub>2</sub> contained in the air and seems to be a significant catalyst in synthesis of organic matter and consequently of grape sugar. Calcium plays a significant role in plant metabolism in the form of organic acid salts. From a strictly enological point of view, its content must be known in wines because of its implication in tartaric precipitations.

One of the aims of this work was to establish a profile as close as possible to reality, so we have tried to measure these elements at all stages from the soil to the grapes, then in the wines, including all the varieties growing in the region.

## MATERIALS AND METHODS

### I- MATERIALS AND REAGENTS

1) Destruction of organic matrix was effected with a microwave digester Maxidigest Mx350 (Prolabo).

**Table I - Program for the mineralization of grapes and soils.**  
**Programme de minéralisation pour les raisins et le sol.**

	Step	Reagents	Volume (ml)	Microwave power %	Time (min)
(a) Grapes*	1	HNO <sub>3</sub> 65 %	25	60	1
	2		0	30	10
	3	H <sub>2</sub> O <sub>2</sub> 35 %	3	15	3
	4	HClO <sub>4</sub> 70 %	3	40	15
(b) Soils	1	HNO <sub>3</sub> 65 %	20	60	1
	2		0	30	10
	3	H <sub>2</sub> O <sub>2</sub> 35 %	3	15	3
	4		0	40	15

\* TEISSEDE *et al.*, 1993

**Table II - Operating conditions for the determinations by atomic absorption spectrophotometry.**  
**Conditions opératoires des dosages par spectrophotométrie d'absorption atomique en flamme.**

Elements	cathode ray lamp	Curent mA	Wavelength (nm)	Slit	Air / acétylène flame	Spectral Buffers (1 g/l)	Calibration range (mg/l)
K	monoelement K	5	769,9	1	oxydizing	*Caesium chloride	0,1-1,5
Na	monoelement Na	5	589,0	0,5	oxydizing	*Caesium chloride	0,1-1,0
Ca chloride	bi-element Ca/Mg 2,5-10,0	10	422,7	0,5	reducing	**Lanthanum	
Mg chloride	bi-element Ca/Mg 0,1-0,5	4	285,2	0,5	oxydizing	**Lanthanum	

\* chloride is a spectral buffer that prevents ionisation of potassium and sodium

\*\* with lanthanum chloride, it is possible to eliminate phosphate interferences during the analysis of calcium.

**Table III - Contents of major elements in soil samples**  
**Teneurs en éléments majeurs dans les échantillons de sol.**

Regions	Pico		Biscoitos Terceira				Graciosa			
	Contents (mg/kg)									
Contents (mg/kg)					*Total	**Solubilized fraction	*Total	**Solubilized fraction	*Total	**Solubilized fraction
Depths cm	10-20	20-40	10-20	20-40	15-20	15-20	20	50	20	50
Potassium	444	524	130	148	211	124	3009	1924	374	202
	808	598	282	247	1357	789	2753	2976	550	573
	425	694	161	233	397	273	1776	1704	222	135
	631	462	217	145	541	240	2240	3726	492	391
	547	197	101	59	438	192	1455	1374	443	424
	719	439	167	172						
	440	390	175	156						
	421	492	124	195						
	779	404	242	171						
	738	405	266	208						
Sodium	1542	1481	136	120	962	43	1168	1231	113	114
	2304	1452	343	132	1104	69	1594	1319	232	265
	1230	1976	107	213	836	43	1075	1312	102	153
	1987	1480	192	121	1264	148	1060	1146	113	168
	1151	1036	117	102	2188	618	1029	1251	35	120
	2928	2706	289	218						
	2055	1436	142	105						
	1154	1486	104	120						
	2660	1492	271	85						
	2209	1573	268	115						
Calcium	6220	5666	3594	3548	5742	3465	1936	2818	1398	2013
	4689	8122	2380	4707	6629	4505	2818	2869	1735	2145
	6350	6154	4670	3208	4399	2593	2387	2765	1495	1818
	5830	6056	3068	3127	7139	5735	1707	1755	1028	1323
	8387	7203	4958	5448	16244	7208	916	1293	475	928
	5574	4720	1990	3370						
	5497	5863	3958	4550						
	4914	5186	3818	4203						
	4770	5304	3560	3139						
	3877	4975	1868	3840						
Magnesium	9330	8510	454	553	9130	103	8700	6180	318	553
	11890	8920	320	773	6630	160	8220	7380	650	753
	9880	9910	700	373	7610	13	9090	7330	298	510
	9830	11070	308	320	6390	190	7290	10230	395	513
	7930	6830	538	585	4900	753	8450	9780	135	263
	9020	6540	240	400						
	9700	7910	493	494						
	7120	9430	375	573						
	7680	10620	300	393						
	6970	9250	283	360						

\* The sample size was 0.5 g in 50 ml.

\*\* The same size was 5 g in 100 ml.

**Table IV - Content of major elements in grape samples**  
**Tableau IV- Teneurs en éléments majeurs dans les échantillons de raisins**

Regions	Pico		Biscoitos-Terceira		Graciosa			
	Variety	Content mg/kg	Variety	Content mg/kg	Variety	Content mg/kg	Variety	Content mg/kg
Potassium	Rio grande (b*)	2467	Seara nova (b)	2367	Verdelho (b)	2300	Arinto (b)	3033
	Periquita (r*)	1833	Verdelho (b)	2467	Arinto (b)	3000	Verdelho (b)	2733
	Saborinho (r)	2133	Arinto (b)	2467	Terrantês (b)	2600	Boal (b)	2333
	Generosa (b)	1533	Terrantês (b)	2333	Verdelho (b)	2600	Terrantês (b)	2733
	Arinto (b)	2533	Seara nova (b)	1867	Verdelho (b)	2933	Boal (b)	2033
	Rufete (r)	2067	Generosa (b)	2533	Verdelho (b)	2733	Tália (b)	2200
	Verdelho (b)	2567	Rio grande (b)	2200	Terrantês (b)	2567		
	C. sauvignon (r)	2200	Agronomica (r)	2233				
	Agronomica (r)	2000	Periquita (r)	1967				
Sodium	Rio Grande (b)	53	Seara Nova (b)	35	Verdelho (b)	27	Arinto (b)	38
	Periquita (r)	42	Verdelho (b)	32	Arinto (b)	47	Verdelho (b)	51
	Saborinho (r)	32	Arinto (b)	36	Terrantês (b)	26	Boal (b)	75
	Generosa (b)	34	Terrantês (b)	35	Verdelho (b)	45	Terrantês (b)	56
	Arinto (b)	26	Seara Nova (b)	49	Verdelho (b)	49	Boal (b)	37
	Rufete (r)	26	Generosa (b)	35	Verdelho (b)	50	Tália (b)	107
	Verdelho (b)	35	Rio Grande (b)	30	Terrantês (b)	85		
	C.sauvignon (r)	32	Agronómica (r)	32				
Agronómica (r)	36	Periquita (r)	26					
Calcium	Rio Grande (b)	297	Seara Nova (b)	452	Verdelho (b)	816	Arinto (b)	708
	Saborinho (r)	604	Arinto (b)	530	Terrantês (b)	780	Boal (b)	602
	Generosa (b)	396	Terrantês (b)	726	Verdelho (b)	798	Terrantês (b)	657
	Arinto (b)	672	Seara Nova (b)	575	Verdelho (b)	869	Boal (b)	395
	Rufete (r)	472	Generosa (b)	264	Verdelho (b)	565	Tália (b)	655
	Verdelho (b)	657	Rio Grande (b)	421	Terrantês (b)	495		
	C.sauvignon (r)	636	Agronómica (r)	690				
	Agronómica (r)	473	Periquita (r)	636				
Magnésium	Rio Grande (b)	106	Seara Nova (b)	93	Verdelho (b)	96	Arinto (b)	135
	Periquita (r)	99	Verdelho (b)	146	Arinto (b)	116	Verdelho (b)	126
	Saborinho (r)	108	Arinto (b)	112	Terrantês (b)	132	Boal (b)	117
	Generosa (b)	85	Terrantês (b)	125	Verdelho (b)	106	Terrantês (b)	126
	Arinto (b)	134	Seara Nova (b)	115	Verdelho (b)	118	Boal (b)	78
	Rufete (r)	98	Generosa (b)	88	Verdelho (b)	137	Tália (b)	121
	Verdelho (b)	120	Rio Grande (b)	88	Terrantês (b)	118		
	C.sauvignon (r)	121	Agronómica (r)	123				
Agronómica (r)	104	Periquita (r)	99					

b : white ; r : red

Metal concentrations were performed using two atomic absorption spectrophotometers: Varian AA-1275 and Varian GBC 306 AA, with hollow cathodic lamps.

2) Stock solutions in ultra pure water contain each 1g/l: K Cl, Na Cl, Mg Cl<sub>2</sub>, Ca NO<sub>3</sub>. Spectral buffers each 50 g/l: Cs Cl<sub>2</sub>, La Cl<sub>3</sub>.

Supra pure grade acids, salts and reagents (Merck) were used.

## II- METHODS

1) Mineralization by humid way: Two programs (table I) were used according to the matrix.

The material used was washed with technical grade boiling nitric acid, then rinsed with ultra pure water.

2) Dissolution: Method of the double acid technique was used for treatment of the whole soils: A mix-

**Table V - Content of major elements in wine samples.**  
**Teneurs en éléments majeurs dans les échantillons de vin.**

Régions	Variety	Pico		Biscoitos-Terceira		Graciosa		
		Content mg/l	Variety	Content mg/l	Variety	Content mg/l	Variety	Content mg/l
Potassium	Rio Grande (b)	1098	*Verdelho (b)		Verdelho (b)	828	*Arinto (b)	
	Periquita (r)	1080	Arinto (b)	769	Arinto (b)	1079	Verdelho (b)	820
	Saborinho (r)	1146	Terrantês (b)		Terrantês (b)	817	Boal (b)	
	Generosa (b)	696			Periquita (r)	501	Terrantês (b)	
	Verdelho (b)	766	*Seara Nova(b)		Verdelho (b)	1189		
	C. Sauvignon (r)	1566	Generosa (b)	1044	Verdelho (b)	899	*Arinto (b)	
	Agronómica (r)	1280	Rio Grande (b)				Verdelho (b)	920
	Seara Nova (b)	1218			*Verdelho(b)	1262	Boal (b)	
			Agronómica( r)	1178	Terrantês (b)		Terrantês (b)	
			Periquita ( r)					
Sodium	Rio Grande (b)	38	*Verdelho (b)		Verdelho (b)	33	*Arinto (b)	
	Periquita (r)	32	Arinto (b)	30	Arinto (b)	126	Verdelho (b)	57
	Saborinho (r)	36	Terrantês (b)		Terrantês (b)	34	Boal (b)	
	Generosa (b)	33			Periquita ( r)	87	Terrantês (b)	
	Verdelho (b)	36	*Seara Nova(b)		Verdelho (b)	55		
	C. Sauvignon (r)	42	Generosa (b)	33	Verdelho (b)	52	*Arinto (b)	
	Agronómica (r)	39	Rio Grande (b)				Verdelho (b)	46
	Seara Nova (b)	32			*Verdelho(b)	141	Boal (b)	
			Agronómica( r)	45	Terrantês		Terrantês (b)	
			Periquita ( r)					
Calcium	Rio Grande (b)	72	*Verdelho (b)		Verdelho (b)	122	*Arinto (b)	
	Periquita (r)	85	Arinto (b)	66	Arinto (b)	122	Verdelho (b)	140
	Saborinho (r)	76	Terrantês (b)		Terrantês (b)	104	Boal (b)	
	Generosa (b)	92			Periquita ( r)	92	Terrantês (b)	
	Verdelho (b)	74	*Seara Nova(b)		Verdelho (b)	74		
	C. Sauvignon (r)	100	Generosa (b)	95	Verdelho (b)	70	*Arinto (b)	
	Agronómica (r)	66	Rio Grande (b)				Verdelho (b)	142
	Seara Nova (b)	65			*Verdelho(b)	130	Boal (b)	
			Agronómica( r)	63	Terrantês (b)		Terrantês (b)	
			Periquita ( r)					
Magnésium	Rio Grande (b)	66	*Verdelho (b)		Verdelho (b)	93	*Arinto (b)	
	Periquita (r)	81	Arinto (b)	107	Arinto (b)	78	Verdelho (b)	81
	Saborinho (r)	92	Terrantês (b)		Terrantês (b)	89	Boal (b)	
	Generosa (b)	79			Periquita ( r)	88	Terrantês (b)	
	Verdelho (b)	86	*Seara Nova(b)		Verdelho (b)	77		
	C. Sauvignon (r)	97	Generosa (b)	76	Verdelho (b)	65	*Arinto (b)	
	Agronómica (r)	96	Rio Grande (b)				Verdelho (b)	81
	Seara Nova (b)	70	Agronómica (r)	87	*Verdelho(b)	121	Boal (b)	
				Terrantês (b)		Terrantês (b)		
			Periquita ( r)					

b : white ; r : red ; \* : lend varieties wines

**Table VI - Statistical results for soils.****Résultats statistiques pour les sols.**

		Mineral elements solid soil content (mg/kg)				Mineral elements solubilized soil content (mg/kg)			
Region		Pico	Bischoitos	Graciosa	p	Pico	Bischoitos	Graciosa	p
Number of samples		20	5	10		20	5	10	
K	m*	527,8	588,8	2293,7	0,0000	179,9	323,6	380,6	0,0015
	sem**	35,3	199,3	248,2		12,7	119,0	47,3	
Na	m	1766,9	1270,8	1218,5	0,0073	165,0	184,2	141,5	0,8408
	sem	124,4	240,2	52,8		16,9	110,2	21,1	
Ca	m	5767,9	8030,6	2126,4	0,0000	3650,2	4701,2	1435,8	0,0000
	sem	251,9	2105,3	223,5		212,1	817,4	164,5	
Mg	m	8917,0	6932,0	8265,0	0,0280	441,8	243,8	438,8	0,0978
	sem	328,5	700,2	394,7		32,2	130,8	60,2	

m: mean ; sem : standard error of the mean; p : level of significance

**Table VII - Statistical results for grapes.****Résultats statistiques pour les raisins.**

		Mineral elements sample content (mg/kg)			
Region		Pico	Bischoitos	Graciosa	p
Number of samples		18	7	6	
K	m	2209,3	2676,1	2510,8	0,0035
	sem	68,2	89,9	155,8	
Na	m	34,8	47,0	60,7	0,0043
	sem	1,7	7,4	10,9	
Ca	m	532,0	726,4	602,8	0,0116
	sem	33,0	52,8	44,7	
Mg	m	109,1	117,6	117,2	0,4176
	sem	4,0	5,3	8,2	

m: mean ; sem : standard error of the mean; p : level of significance

ture in equal parts of 100 ml of hydrochloric acid 0.05 N and sulphuric acid 0.025 N is added to earth (5 g). The solution is stirred (15 min, 180 rpm).

3) Determination: Levels of the four elements were measured by atomic absorption in flame (table II).

Determinations in wine were made after suitable dilutions and for grapes (15 g samples of fresh weight) on the acid solution (program a) brought back to 50 ml at the end of the mineralization process.

For soils: two determinations were made. The first one on the acid destruction liquid (program b) of the samples (0.5 g) brought back to 50 ml, and the second one on the liquid obtained after dissolution by double acid technique.

4) Statistic processing was carried out by STAT-GRAPHICS software. Variance analysis for one factor (factor region) were done for each element measured in soil, grape and wine. The differences between average levels obtained by region is significant for  $p < 0.05$ .

## RESULTS

### I - MINERAL CONTENTS

Potassium, calcium, magnesium contents in soils, grapes and wines in the three regions of the Azores (Pico, Bischoitos/Terceira and Graciosa) analysed for this study are listed in tables III, IV and V.

### II - STATISTICAL STUDY RESULTS

The results, for soils, grapes and wines are reported in tables VI, VII and VIII.

Concerning soils, a first variance analysis test was calculated to determine if there was a significant difference between the contents of the elements assessed at different sampling depths: under 20 cm or above 20 cm. As the test did not show any significant differences, we carried out the study by mixing the results from both depths.

For each element studied, the variance analysis gave significant levels between the regions: for soils, signi-

**Table VIII - Statistical results for wines.****Résultats statistiques pour les vins.**

Regions		Mineral elements sample content mg/l			p
		Pico	Biscoitos	Graciosa	
Number of samples		11	7	2	
K	m	1076,5	939,3	870,0	0,3960
	sem	77,1	98,5	50,0	
Na	m	36,0	75,4	51,5	0,0221
	sem	1,4	16,5	5,5	
Ca	m	77,6	102,0	141,0	0,0004
	sem	4,0	9,1	1,0	
Mg	m	85,2	87,3	81,0	0,8529
	sem	3,7	6,7	0,0	

m: mean ; sem : standard error of the mean; p : level of significance

ficant differences were obtained between the three wine regions for potassium, sodium, magnesium and calcium concerning the whole content. For the solubilized content, two elements out of the four are not significant: sodium and magnesium. However, some elements dominate in a certain region: Pico is characterized by high sodium and magnesium rates. Biscoitos is characterized by high calcium rates and Graciosa by high potassium rates.

For grapes, significant differences between the three wine regions were obtained for potassium, sodium and calcium.

There is only one non-significant difference for magnesium. The dominating elements by region are potassium and calcium for the Biscoitos region, sodium for the Graciosa region. The lowest contents for the four elements were obtained for the Pico region.

For wines, significant differences between the three regions were obtained for sodium and calcium, though not significant for potassium and magnesium.

The wines for the Biscoitos region have a higher sodium content; those from the Graciosa region the highest calcium. The wines from the Pico region have the lowest rates for the four elements.

## DISCUSSION AND CONCLUSION

We observe the following fact: the soils are different, each being characterized by one or two elements. Vine stocks have responded selectively to the soils. Yet, the wines have not always followed the grape richness.

Soil is characterised by its physical structure, its pH plays a significant role in dissolving metals and we know that the three Azores Islands studied are made of volcanic soils, almost exclusively composed of pri-

mary magmatic rocks . The climate, influenced by latitude, insularity and relief, is temperate and oceanic with a low annual range of temperature. Moreover, the winds are strong , heavy with salt. Why is there, thus, a difference between the elements in the three regions? For potassium, the richness of the Graciosa region can be explained by the fact that the vineyards are older and consequently more evolved, having undergone a more significant potassium dissolution in the rocks by the hydrolysing action of water.. Moreover, the island contains clay and GALET (1976) asserts that , in clayey soils, the content of potash increases with that of clay.: from 100 to 180 ppm potassium for clay percentages varying between 10 and 25 %. For sodium, the high rates in the Pico region can be explained by its greater exposure to spray and strong winds, both laden with sodium chloride from the ocean. For magnesium, the richness can result from the density of this element in the lithosphere as it is an element which ranks 8th with a proportion of 0.14 % in the seas and oceans (Pascal). These contents, although higher on Pico island, are significant for the three wine regions and concur with the results reported in a thesis, MADRUGA (1995) on the soils in the Azores ranging from 1g/kg to 45 g/kg. For calcium, the presence of this element must be due to limestone fertilizers. In fact, as the soils are volcanic and not calcareous, they have a very acidic pH which must be modified to cultivate the vine.

The quantities of these four elements in their solubilized form show the same profile as when found in the soils, potassium particularly corresponds to the contents found in the Pico region from 50 to 155 ppm (RIBEIRO DE LIMA, 1992). We observe however the greater solubility of calcium. Soluble calcium indeed accounts for 50 % of the total amount of calcium in the three islands, whereas magnesium accounts only for 5 % on average, sodium 8 %, and potassium 34 %.

We can conclude that the three wine regions have different soils. This information is significant because it will enable us to make up the deficits or to reduce the excess, in order to improve vine management.

For grapes, there is no correlation between their content and the corresponding soil content. This can be explained first by the difficulty in sampling, then by the representative character of the sample. Soil is an important but not the only influential factor: environment, climate and vine cultivation must be taken into account. Studies have been carried out (FREGONI *et al.*, 1999) on vine nutrition in acidic and sub-acidic soils, conditions found in the three regions studied, with average pH 6 for the Pico region, 5.3 for the Biscoitos region and 5.6 for the Graciosa region. This study reports that acidic pH favours the absorption of micro-elements. This phenomenon is lessened by different selectivities according to rootstocks. Our results do not seem to confirm this hypothesis, but it is true that pH are slightly acidic, never below 5, and that we do not know the rootstocks.

Indeed, grapes from the Biscoitos region, which is the more acidic with pH = 5.3, have the highest contents in potassium, magnesium and calcium.

We can conclude that, despite all the influences, the vinestock has its own, very complex autonomy, which allows it to choose what is good for the plant and the development of its fruits. For example, we know that the vine has significant needs in potassium from flowering to fruit set, so there is a significant potassium migration from the leaves, where it is stored, to the grapes. We know also that the lack of potassium in soils corresponds to a higher absorption of calcium or of magnesium counter-balancing organic anions (GALET, 1976).

For the wine, there is no correlation between grapes and wines, nor between wines and soils. This can be explained by the fact that the wines studied were generally pure varietals, but some of them were blended wines. In this case too many parameters are to be taken into account to find any correlation. What is interesting here, is to compare our results with those obtained in other countries. If for example, we compare the results reported by CABANIS *et al.* (1998) for Europe, we observe that for potassium (970 mg/l) and for magnesium (90 mg/l), our average contents, respectively 962 and 84.5 mg/l are similar to Europe. Calcium, 70 mg/l and sodium 25mg/l for Europe are higher in the Azores wines, respectively 106.8 and 54.2 mg/l.

For calcium, we find similar contents to continental Portugal (CURVELO-GARCIA and GHIRA, 1978, 1979a, b, and 1987). We think that in this case, high

calcium content is more likely due to the contact with rough concrete vats. Calcium contents in Portugal must be lower now because this country has modernized its cellar equipment. For sodium, MARQUES (1997) had found values from 37 to 56 mg/l in the Pico region. The effects of sea spray are more important on the islands or the coasts than in the continent. Our results confirm this phenomenon and are consistent with Fernandez (1994), sodium 142 mg/l in the Canary islands, and BERG *et al.* (1979) reporting an average content of 88 mg/l in California wines. For this element, there is an O.I.V limit of 60 mg/l of excess sodium. Calculations made on the highest sodium contents show that only a small quantity of wine was situated beyond the authorized limit.

In conclusion, for wines, excess sodium must be carefully controlled as well as calcium content. If the latter is not harmful to the health, it is harmful to the chemical stability of wines.

## REFERENCES

- BERG H.W., AKYOSHI M. and Amerine M.A., 1979. Potassium and sodium content of California wines. *Am. J. Enol. Vitic.*, **30**, 55-57.
- CABANIS J.C., CABANIS M.T., CHEYNIER V. AND TEISSEDE P.L., 1998. Composition Tables. In : *Flanzy C., Œnologie. Fondements scientifiques et technologiques* (pp 315-336). Paris : Lavoisier, Tec & Doc,
- CURVELO-GARCIA S., 1978. Caracterização Enológica da Região Demarcada do Dão. *De Vinea et Vino, Portugaliae Documenta*, 2: 2-14, Instituto Nacional de Investigação Agrária.
- CURVELO-GARCIA A.S. and GHIRA J., 1979a. *Caracterização Enológica das Principais Regiões Vitícolas do País; II. Região do Oeste*. Instituto Nacional de Investigação Agrária. Dois Portos.
- CURVELO-GARCIA A.S. and GHIRA J., 1979b. *Caracterização Enológica das Principais Regiões Vitícolas do País; III. Região do Cartaxo*. Instituto Nacional de Investigação Agrária. Dois Portos.
- CURVELO-GARCIA A.S. and GHIRA J., 1987. *Caracterização Enológica das Principais Regiões Vitícolas do País; IV. Região de Pinhel*. Instituto da Vinha e do Vinho. Sacavém.
- FREGONI M. and BAVARESCO L., 1999. *1° Symposium international sur la viticulture en sols acides*. INST CNRS.
- GALET P., 1976. *Précis de Viticulture*, 3<sup>e</sup> édition. ed. Galet, Dehan, Montpellier.
- HERNADEZ G.G., 1994. Caracterización físicoquímica y sensorial de los mostos y vinos tintos de la parte oriental de la denominación de origen Tacaronte-



- Acentejo de Tenerife. *Thesis Doctoral*, Universidad de La Laguna, La Laguna.
- MADRUGA J., 1995. Caracterização e constituição dos horizontes plácicos em solos do Arquipélago dos Açores. *Thesis de Doutoramento*, Universidade dos Açores, Angra do Heroísmo.
- MARQUES T.S.C.L., 1997. Contribuição para a caracterização físico-química e sensorial do vinho Licoroso do Pico. *Relatório de estágio de licenciatura*. Universidade dos Açores, Angra do Heroísmo.
- OIV (1990). *Recueil des Méthodes Internationales d'Analyse des Vins et des Moûts*. Paris.
- PASCAL (1963). *Nouveau traité de chimie minérale*. Paris, ed. Masson et Cie,
- RIBEIRO DE LIMA M.T, 1992. Caracterização físico-química do vinho « Verdelho do Pico », tipo aperitivo. *Trabalho de síntese para as provas de aptidão pedagógica e capacidade científica*, Universidade dos Açores, Angra do Heroísmo.
- TEISSEDRE P.L, CABANIS M.T. and CABANIS J.C, 1993. Comparaison de deux méthodes de minéralisation en vue du dosage du plomb par spectrométrie d'absorption atomique électrothermique. Application à des échantillons de sols, feuilles de vignes, raisins, moûts, marcs et lies. *Analisis*, **21**, 249-254.

*Manuscrit reçu le 24 mars 2003 ; accepté pour publication le 23 mai 2003*