Accumulation and Distribution Pattern of Macro- and Microelements and Trace Elements in *Vitis vinifera* L. cv. Chardonnay Berries

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ABSTRACT: This paper describes the accumulation pattern of 42 mineral elements in *Vitis vinifera* L. berries during development and ripening and their distribution in berry skin, seeds, and flesh around harvest time. Grape berries were sampled in two different vineyards with alkaline soil and analyzed using a ICP-MS. Although elemental amounts were significantly different in the grapes from the two vineyards, the accumulation pattern and percentage distribution in different parts of the berries were generally quite similar. Ba, Eu, Sr, Ca, Mg, Mn, and Zn accumulate prior to veraison. Al, Ce, Dy, Er, Ga, Gd, Ho, La, Nd, Pr, Sm, Sn, Zr, Th, Tm, U, Y, and Yb accumulate mainly prior to veraison but also during ripening. Ag, As, B, Cd, Cs, Cu, Fe, Ge, Hg, K, Li, Na, P, Rb, Sb, Se, and Tl accumulate progressively during growth and ripening. With regard to distribution, Ba, Ca, Eu, Fe, Mn, P, Sr, and Zn accumulate mainly in the seeds, Al, B, Ga, Sn, and the rare earths analyzed, except for Eu, accumulate mainly in the skin, and Ag, As, Cd, Cs, Cu, Ge, Hg, K, Li, Mg, Na, Rb, Sb, Se, Th, Tl, U, and Zr accumulate mainly in the flesh. A joint representation of the accumulation and distribution patterns for the elements in the berry is also given.

KEYWORDS: *Vitis vinifera* L., Chardonnay, grape, ICP-MS, mineral elements, skin, seeds , flesh

■ INTRODUCTION

Knowledge of the accumulation of mineral elements in plants and their distribution in the different parts of fruit has been considered to be essential for biochemical and physiological studies[1] and is a fundamental tool for supporting traceability studies on the geographical origin of food commodities,[2,3] table grapes and wine included.[4−11]

The presence of each mineral element in soil and plants, above all trace and ultratrace elements, is considered to be closely tied to the geological composition of the underlying mother rock, the physical and chemical properties of the soil, and the specific ability of the plant to take up and accumulate each individual element.[12] Biological and biochemical research generally defines trace elements as those elements present in very low concentrations, below 0.01% in the organism.[13] Sometimes micronutrients such as Zn, Mn, B, and Cu are also included among trace elements; however, strictly speaking, trace elements should be defined as elements not identified as essential for living beings.[14] Besides known nutrients (N, P, K, Ca, Mg, S, B, Zn, Cu, Mn, Fe, Ni, Mo, and Cl[15,16]) and the so-called "beneficial elements" (e.g., Na, Si, Co[15]), many others would seem to promote different physiological processes, although absorption and action mechanisms and specific roles, as well as levels of concentration and distribution in the different parts of the plant, are not yet known or are still unclear. The number of elements assumed to have a function or a physiological role has increased over the years as a consequence of improvements in analytical techniques and new research.[13,15,16] Some trace elements such as Li, Ni, Rb, Se, V, and rare earths are reported to have positive effects on growth and production in some plant species. Ag, Au, Br, Cd, F, Hg, Pb, I, and U are reported to affect the permeability of the plasma membrane, whereas other elements, such as Se, As, Sb, Te, W, Al, Be, Zr, Cs, Rb, Li, Sr, and rare earths, can compete with or substitute essential elements in different molecules and enzymes. Trace elements and nutrients may have synergic or antagonistic interaction and be beneficial or phytotoxic depending on their concentration level.[12]

Several basic studies have investigated the principal macroelements;[17−21] however, for most microelements and trace elements there is a lack of in-depth knowledge about their biological role and concentration in the vine. With regard to 10 macro- and microelements, Rogiers et al.[22] studied patterns in accumulation and partitioning in berry tissues during grape ripening. They divided these elements into two groups according to the accumulation pattern: those that accumulate throughout berry growth and ripening (B, Cu, Fe, K, Mg, P, and S, phloem-mobile elements) and those that accumulate mostly prior to veraison (Ca, Mn, and Zn, xylem-mobile minerals). They observed that flesh and skin were the strongest sinks for B and K, whereas seeds were the strongest sink for Ca, Mn, P, S, and Zn. With regard to rare earth elements, their content in soil, grapes, must, and wine and their distribution in the berry were investigated.[23,24] The rare earth elements profile, after normalization against Ce, was similar from soil to wine, at least for rare earths with lower atomic weight, although absolute contents

decreased significantly, by about 4 orders of magnitude.[23] In Chardonnay berries, percentage content was in decreasing order in skin, flesh, and seeds for Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, and Yb, whereas Eu was higher in the seeds.[24] More recently, Young et al.[25] studied the profile of 18 trace elements (B, Mn, Fe, Cu, Zn, Cr, Sr, Ba, Mo, Zr, Pd, Cd, Co, Ni, Ga, Ge, Tl, and U) and 15 rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in the berry tissues of Italian Riesling, Marselan, and Cabernet Sauvignon, observing that the former were located in decreasing order in seeds, skin, and flesh, whereas rare earth elements were located mainly in the skin, with differences among the three cultivars. Clearly, greater attention has traditionally been paid to heavy metals (e.g., Cd, Cu, Pb, and Zn) due to their toxicological and environmental impacts.[4,26−28]

As a contribution toward understanding the phenomena on which the geographical traceability of the soil−grapes−wine production line is based, this paper describes the content of 55 macro- and microelements and trace elements in *Vitis vinifera* L. cv. Chardonnay grape berries and the changes during development and ripening. Moreover, mineral element distribution in berry skin, seeds, and flesh around harvest time is defined.

■ MATERIALS AND METHODS

Chemicals. Concentrated nitric acid (ultrapure, 96.5%) was purchased from Merck (Darmstadt, Germany); ultrapure Milli-Q water (18.2 MΩ, Millipore, Bedford, MA) was used for all standard solution and sample preparations. Al, Ca, Fe, K, P, and Rb standard solutions were purchased from CPI International (Santa Rosa, CA); Cs standard solution was from Ultra Scientific Italia srl (Bologna, Italy); Cu, Mg, Na, and Sr standard solutions and ICP multielement standard solution VI were from Merck; Hg standard-2A solution and multielement calibration standard-1 and -3 solutions were from Agilent Technologies (Tokyo, Japan); the ICP-MS calibration standard 4 solution and Sc, Re, Rh, and Tb standard solutions were from Aristar BDH (Poole, U.K.). Certified reference materials NIST 1640 Natural Water and NIST 1548a Typical Diet were supplied from the National Institute of Standards and Technologies (Gaithersburg, MD). All of the materials used were washed with 5% (v/v) HNO₃ and rinsed with Milli-Q water before use.

Plant Material and Sampling. The grapes were collected from *V. vinifera* L. cv. Chardonnay, clone ENTAV 95, grafted onto rootstock 3309 (*V. riparia* × *V. rupestris*) vines. The vines were grown in 20-year-old, WSW exposed and Guyot-trellised vineyards (1.6 × 1 m) located in S. Michele all'Adige (SM; 289 m asl; latitude 46° 11′ 34″ N; longitude 11° 08′ 19″ E) and Faedo-Maso Togn (MT; 723 m asl; 46° 11′ 49″ N; 11° 10′ 14″ E), Trentino, in northeastern Italy. The SM vineyard had a silt loam, very calcareous, alkaline soil, whereas the MT vineyard had a sandy loam, alkaline soil, notably calcareous with low active lime. Both were grass-covered and managed without manure treatments. In each vineyard, four plots (considered as replications) of 20−50 grapevines each were defined at least 5 m away from the edges. In 2006, 11 (in SM) and 12 (in MT) sampling dates were scheduled from berry set (about 40 days prior to veraison) until 2−3 weeks after technological ripeness (60 days after veraison) every 2 weeks until veraison and weekly thereafter. A period of drought in July led to a delay in berry development in the MT vineyard, for which a 12th sampling date was required. One hundred berries were picked from 20 bunches at random for each sampling date and plot (4 replicates of 100 berries for each vineyard). These samples were used for the analysis of the mineral element content of the whole berry. In the last five sampling dates, starting from about 30 days after veraison, a further 200 berries were collected weekly: 100 to quantify elements in skin and seeds (further 4 replicates: 100 berries/vineyard)

and 100 to analyze the basic composition of the juice (further 4 replicates: 100 berries/vineyard). Only undamaged and sound berries were sampled, cutting the pedicel just upon the base.

Sample Preparation. Grape samples were processed within 3 h after picking. The berries used for the mineral element analysis were washed with a 1% (v/v) HNO₃ solution, rinsed with Milli-Q water, and blotted with clean paper. To establish the content in the whole berry, 100 berries were weighed, frozen (−20 °C), homogenized using an Ultraturrax T25 (dispersion tool: ∅ 15 mm; IKA-WERKE, Staufen, Germany), and acid digested using a microwave system (Mars Express, CEM, Matthews, NC) equipped with 75 mL PTFE vessels. Four milliliters of HNO₃, 5 mL of Milli-Q water, and 1 mL of Re internal standard solution were added to 2.5 g of homogenized sample (fresh weight, FW). Digestion conditions were as follows: 0 min, 25 °C; 8 min, 100 °C; 13 min, 100 °C; 23 min, 150 °C; 28 min, 150 °C; 40 min, 210 °C; 50 min, 210 °C. To establish the content in berry skin, seeds, and flesh, 100 fresh berries were weighed and manually peeled. Skins were rasped to remove flesh, weighed, frozen, and homogenized. Seeds were manually cleaned to remove flesh residues, blotted with clean paper, weighed, frozen, and homogenized, following the addition of an equal weight of ultrapure water. Seed and skin samples (1.5 g FW) were acid digested as described above for whole berry. The mineral content in flesh was calculated as the difference between the whole berry and skin plus seeds.

Mineral Element Analysis. Analysis of 55 mineral elements was performed using a quadrupole inductively coupled plasma mass spectrometer (ICP-MS, 7500ce; Agilent Technologies, Tokyo, Japan) equipped with an autosampler ASX-520 (Cetac Technologies Inc., Omaha, NE), a MicroMist nebulizer, a quartz Fassel-type torch, and Ni cones. An Octopole Reaction System was employed to remove polyatomic interferences, using H₂ as reaction gas for the analysis of Ca, Ga, and Se, and He as collision gas for the analysis of As, Cu, Eu, Fe, K, Mg, Na, V, and Zn. The isotopes detected were as follows: ¹⁰⁹Ag, ²⁷Al, ⁷⁵As, ¹⁹⁷Au, ¹¹B, ¹³⁷Ba, ⁹Be, ²⁰⁹Bi, ⁴⁰Ca, ¹¹¹Cd, ¹⁴⁰Ce, ¹³³Cs, ⁶³Cu, ¹⁶³Dy, ¹⁶⁷Er, ¹⁵¹Eu, ⁵⁶Fe, ⁷¹Ga, ¹⁵⁷Gd, ⁷⁴Ge, ¹⁷⁸Hf, ²⁰²Hg, ¹⁶⁵Ho, ¹⁹³Ir, ³⁹K, ¹³⁹La, ⁷Li, ¹⁷⁵Lu, ²⁶Mg, ⁵⁵Mn, ²³Na, ⁹³Nb, ¹⁴⁶Nd, ³¹P, ²⁰⁶Pb + ²⁰⁷Pb + ²⁰⁸Pb, ¹⁰⁸Pd, ¹⁴¹Pr, ⁸⁵Rb, ¹⁸⁵Re, ¹²¹Sb, ⁷⁸Se, ¹⁴⁷Sm, ¹¹⁸Sn, ⁸⁸Sr, ¹⁸¹Ta, ¹²⁶Te, ²³²Th, ²⁰⁵Tl, ¹⁶⁹Tm, ²³⁸U, ⁵¹V, ¹⁸⁴W, ⁸⁹Y, ¹⁷¹Yb, ⁶⁶Zn, and ⁹⁰Zr. The instrument was tuned with a 1 μg/L solution of Li, Y, Ce, and Tl to have a relative standard deviation < 3%, an oxide % < 1, and a doubly charged % < 2. A solution of Sc, Rh, and Tb (3 mg/L) was used as the online internal standard. The instruments were calibrated daily against external certified standard solutions. Each analytical sequence of samples included a blank (ultrapure water digested as the other samples) and one blank spiked with known amounts of the aforementioned standards. The accuracy of the method was checked against two reference materials (NIST 1640 Natural Water and NIST 1548a Typical Diet) with recovery of between 82 and 110% for all certified elements, except for Pb in NIST 1548a (76%). These recoveries can be considered as acceptable for the purpose of this research. For each element, the detection limit (DL) was calculated as 3 times the standard deviation of the signal of the blank prepared and analyzed 10 times.

Basic Composition of Grape Juice. One hundred berries were pressed (3 bar) and filtered on cotton wool to obtain the juice. The basic composition (% of total soluble solids, as °Brix; pH; titratable acidity; malic and tartaric acids) of the grape juice was measured using a Fourier transform infrared spectrometer (FT-IR Grapescan 2000; FOSS, Hillerød, Denmark) to assess the progress of ripening.

Data and Statistical Analysis. With regard to the content of mineral elements in the two vineyards and in the three parts of the berry, a main effect analysis of variance (ANOVA with *t* test) and Tukey's test were performed. Interactions were not considered. Normal distribution and homogeneity of variance were verified using the Kolmogorov−Smirnov ($p < 0.05$) and Levene tests ($p < 0.01$), respectively. The
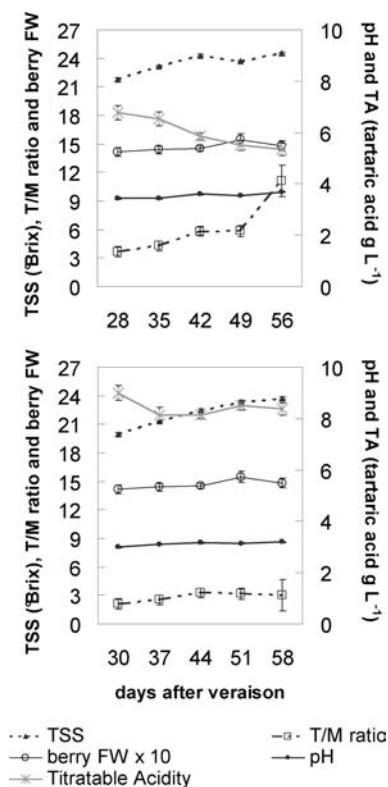
Figure 1. Enological parameters in juices and fresh weight of berries from the San Michele (SM, top) and Faedo-Maso Togn (MT, bottom) vineyards. The values given are the means of four plots. FW, fresh weight; TSS, total soluble solids; T/M ratio, tartaric to malic acid ratio; TA, titratable acidity. Bars indicate the standard error of the mean.

accumulation pattern for each element (y) during berry development and ripening (t) was modeled with a logistic function, as suggested for K and total soluble solids by other authors:[29,30]

$$y = k(1 + e^{-\alpha(t-\beta)})^{-1} \qquad (1)$$

k is the asymptote of the function, α is the slope at origin, and β is the inflection point, in days after veraison. Two other useful parameters for describing the accumulation pattern were calculated: (1) preveraison storage %, which is the percentage content accumulated until veraison as compared to the content measured on the last sampling date, and (2) 90% k, which is the time, in days after veraison, at which the element reached a concentration equal to 90% of k. The first represents mineral accumulation amount until complete development of the seeds and is taken as an evaluation of accumulation earliness, whereas the second is taken as an evaluation of the time needed for a nearly complete uptake. To group elements on the basis of similar accumulation or distribution patterns, cluster analysis was applied to accumulation parameters (α, β, preveraison storage %, and 90% k) and to the percentage distribution of elements in the three parts of the berry (skin, seeds, and flesh) for the two vineyards. Cluster analysis was performed using the Euclidean distance and complete linkage options. All analyses and tests were performed with Statistica 8.0 (StatSoft Inc., Tulsa, OK).

■ RESULTS AND DISCUSSION

Grape Composition at Ripeness. All of the grape samples of the last five sampling dates, collected weekly in the two vineyards (San Michele, SM; and Faedo-Maso Togn, MT)

Table 1. Elemental Content in Technologically Ripe Berries[a]

	SM + MT (μg/kg FW)			SM + MT (μg/kg FW)	
	mean	SE		mean	SE
Ag	1.178	0.022	Li	1.030	0.064
Al	371	15	Mg	134092	1350
As	0.399	0.025	Mn	1333	28
B	3764	143	Na	1671	32
Ba	487	18	Nd	0.488	0.021
Ca	299009	7181	P	191902	3468
Cd	0.085	0.004	Pr	0.113	0.005
Ce	0.955	0.043	Rb	890	103
Cs	5.198	0.964	Sb	0.252	0.019
Cu	860	21	Se	0.317	0.017
Dy	0.035	0.002	Sm	0.086	0.004
Er	0.019	0.001	Sn	3.397	0.171
Eu	0.045	0.002	Sr	461	30
Fe	1534	48	Th	0.269	0.013
Ga	0.098	0.004	Tl	0.053	0.005
Gd	0.063	0.003	Tm	0.005	0.001
Ge	0.039	0.003	U	0.021	0.001
Hg	0.259	0.008	Y	0.121	0.006
Ho	0.007	0.000	Yb	0.018	0.001
K	2469670	48405	Zn	457	14
La	0.418	0.018	Zr	2.389	0.192

[a] SM + MT = means of the two vineyards, $N = 40$.

starting from about 30 days after veraison, had ripeness levels (19.9−24.5 °Brix) consistent with the production regulations of Trentino Chardonnay Protected Designation of Origin (Figure 1), so they can be considered to be technologically ripe. SM vineyard samples reached a higher ripeness level, as shown by the higher total soluble solids and pH and lower levels of titratable acidity and particularly malic acid. The tartaric/malic acid ratio increased from 3.7 to 10.7 in SM grapes and from 2.1 to 3 in MT grapes, showing a clearer and more rapid degradation of malic acid in the first case (Figure1).

Of the 55 elements analyzed in the grapes, the following 42, listed in decreasing order of mean concentration, were quantified: K, Ca, P, Mg, B, Na, Fe, and Mn were higher than 1000 μg/kg FW; Rb, Cu, Ba, Zn, Sr, and Al ranged between 1000 and 100 μg/kg FW; Cs, Sn, Zr, Ag, and Li ranged between 10 and 1 μg/kg FW; Ce, Nd, La, As, Se, Th, Hg, Sb, Y, Pr, Ga, Sm, Cd, Gd, Tl, Eu, Ge, Dy, U, Er, Yb, Ho, and Tm were under 1 μg/kg FW. The following 13 elements were always below the method's DL: Au (<0.05 μg/kg FW), Be (<0.02 μg/kg FW), Bi (<0.01 μg/kg FW), Hf (<0.04 μg/kg FW), Ir (<0.04 μg/kg FW), Lu (<3 μg/kg FW), Nb (<1.6 μg/kg FW), Pb (<0.88 μg/kg FW), Pd (<0.01 μg/kg FW), Ta (<2 μg/kg FW), Te (<0.02 μg/kg FW), V (<0.03 μg/kg FW), and W (<8 μg/kg FW) (Table 1).

Accumulation Pattern for Mineral Elements in the Berry. The 42 analytically detectable elements were quantified in berries during development and ripening in both vineyards except for Tl, which is present above the DL only in the MT samples. Because of the increase in size and weight of berries over the season, the concentration pattern of the element by fresh weight is different from that of the content per berry; however, we preferred the latter as it was considered to be more suitable for describing

(a)

Figure 2. Continued

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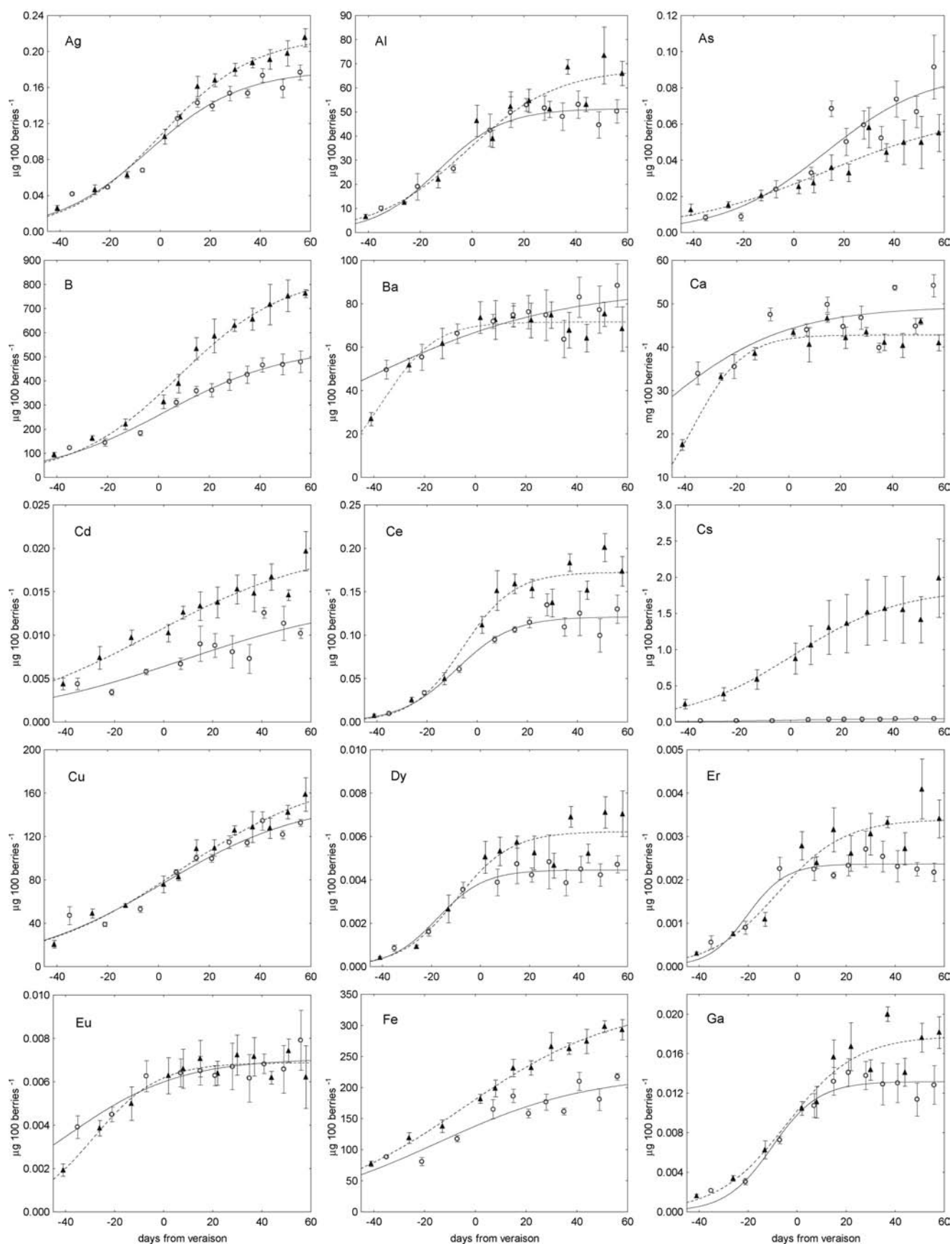
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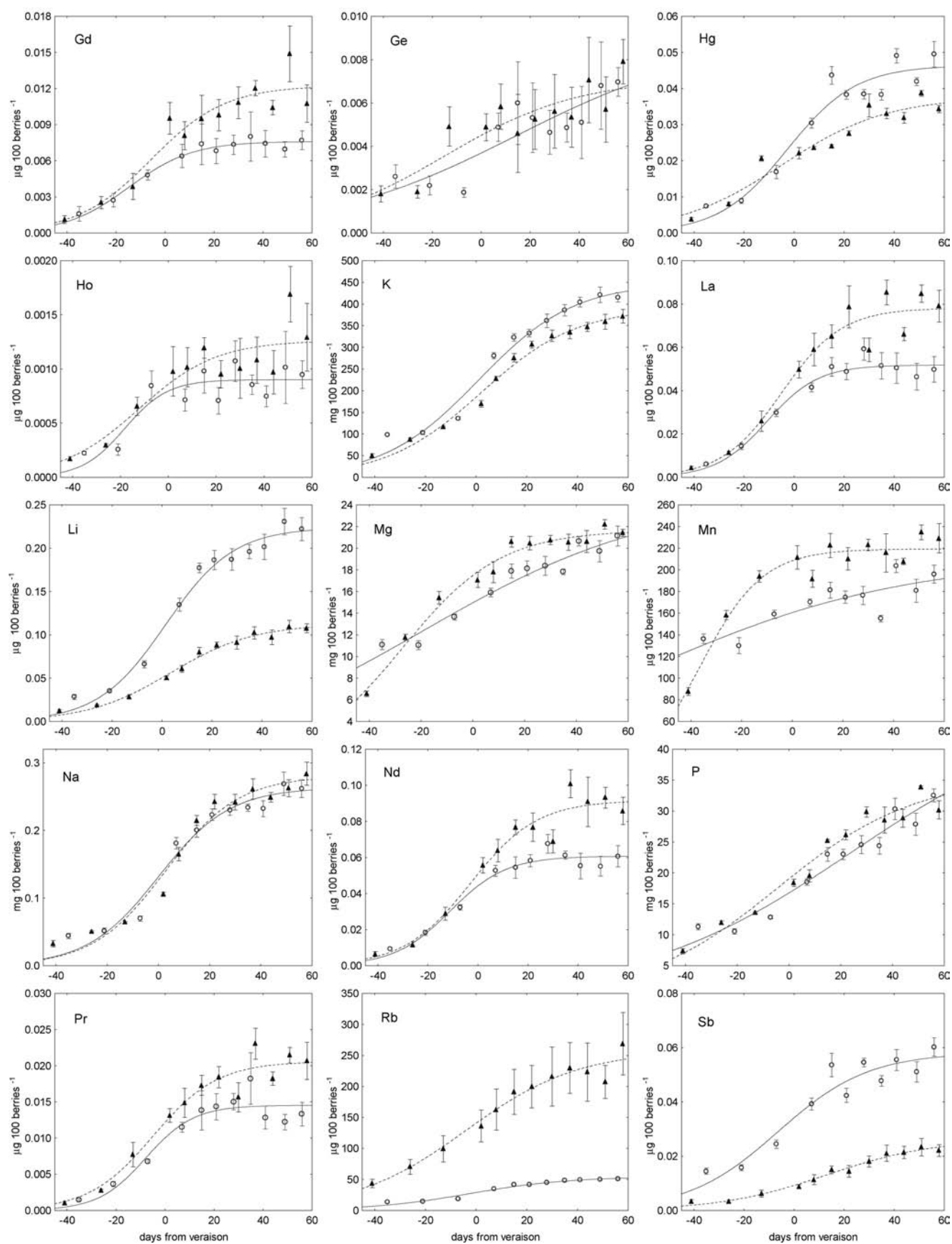
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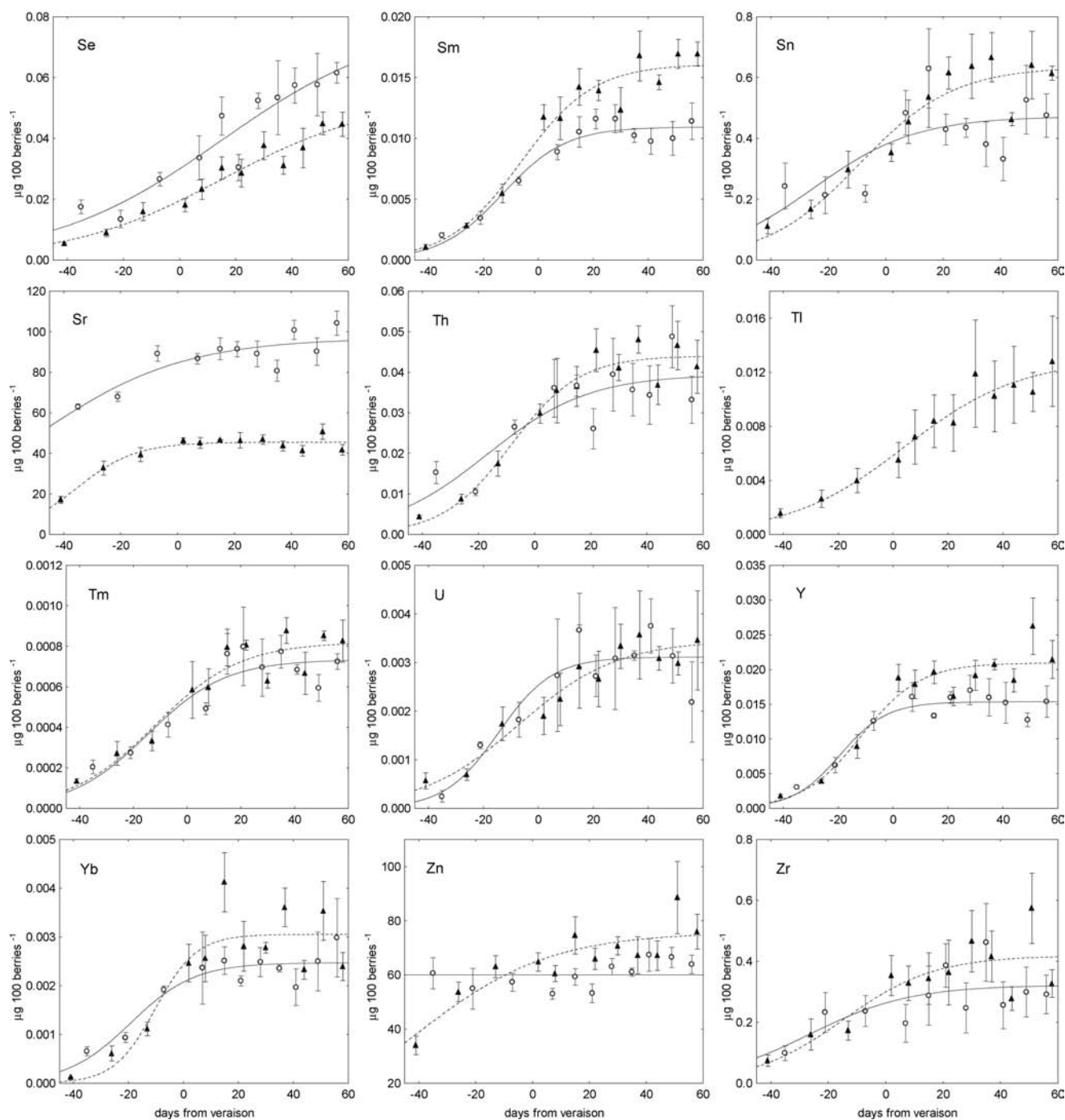
Figure 2. Experimental data and fitted logistic model of the content (μg or mg per 100 berries) of 42 macro- and microelements and trace elements during development and ripening in whole berries collected in SM (hollow circle and continuous line) and MT (full triangle and dotted line) vineyards. Bars indicate the standard error of the mean ($N = 4$, mean of 400 berries). For fitted model parameters see Table 2.

translocation phenomena and more interesting from a physiological point of view.

Generally, the accumulation patterns were well modeled by the logistic function (Figure 2) as indicated by the high regression coefficients obtained (Table 2). Only the Ca, Sn, and Zr of SM grapes had R^2 values <0.7. For Sn and Zr this is probably due

to the combination of several factors, such as the low sensitivity of the method for these elements and possible incomplete removal of organometallic pesticides (e.g., the organotin $C_{60}H_{78}OSn_2$ Fenbutatin-oxide) by the washing process with diluted mineral acid. With regard to Ca, results show that even the first sampling date in the SM vineyard (35 days prior to veraison) was already

Table 2. Parameters for Logistic Function and Other Parameters for the Accumulation Pattern of Each Element for the Two Vineyards[a]

	(A) SM Vineyard								
	k (μg per 100 berries)		α (μg per 100 berries per day)		β (days from veraison)				
element	mean	SE	mean	SE	mean	SE	R^2	preveraison storage %	90% k
Ag	0.179	0.010	0.054	0.009	−5	4	0.964	57	36
Al	51.39	2.15	0.08	0.017	−13	3	0.945	75	15
As	0.089	0.021	0.049	0.021	13	13	0.867	34	58
B	543	0.036	0.041	0.005	3	4	0.982	54	56
Ba	87.49	13.98	0.025	0.017	−46	11	0.776	76	40
Ca	49370	4.29	0.04	0.034	−53	19	0.554	82	1
Cd	0.014	0.007	0.026	0.017	8	43	0.78	52	92
Ce	0.121	0.006	0.089	0.022	−8	3	0.939	63	16
Cs	0.046	0.003	0.054	0.010	−4	4	0.956	59	37
Cu	154	0.022	0.036	0.009	2	10	0.941	56	64
Dy	0.004	0.000	0.105	0.025	−18	2	0.941	82	3
Er	0.002	0.000	0.127	0.041	−20	3	0.901	101	−3
Eu	0.007	0.000	0.044	0.018	−39	6	0.83	76	11
Fe	222	0.037	0.033	0.014	−15	12	0.848	64	51
Ga	0.013	0.000	0.105	0.024	−10	2	0.953	76	11
Gd	0.008	0.000	0.077	0.011	−15	2	0.974	75	14
Ge	0.009	0.006	0.025	0.019	14	56	0.752	38	101
Hg	0.046	0.003	0.073	0.018	−3	4	0.931	51	28
Ho	0.001	0.000	0.111	0.056	−18	5	0.776	84	2
K	449228	26.6	0.053	0.008	1	3	0.972	53	42
La	0.052	0.002	0.098	0.021	−11	2	0.956	77	12
Li	0.224	0.009	0.073	0.010	1	2	0.98	48	31
Mg	24825	3.74	0.022	0.007	−19	14	0.949	71	79
Mn	211	0.054	0.019	0.019	−60	17	0.706	82	55
Na	263	0.013	0.072	0.013	0	3	0.966	50	31
Nd	0.061	0.002	0.089	0.018	−11	3	0.956	73	14
P	46613	16.29	0.024	0.008	24	32	0.945	52	116
Pr	0.015	0.001	0.103	0.036	−8	4	0.895	75	14
Rb	54.37	3.43	0.051	0.009	−3	4	0.966	57	41
Sb	0.058	0.005	0.055	0.015	−6	5	0.914	57	33
Se	0.079	0.024	0.033	0.013	15	22	0.897	49	82
Sm	0.011	0.000	0.087	0.019	−13	3	0.947	72	12
Sn	0.472	0.074	0.056	0.049	−25	12	0.458	80	14
Sr	96.94	6.8	0.039	0.022	−50	12	0.733	81	7
Th	0.039	0.005	0.055	0.03	−17	9	0.707	85	23
Tl	—	—	—	—	—	—	—	—	—
Tm	0.001	0.000	0.069	0.025	−15	5	0.845	74	17
U	0.003	0.000	0.102	0.047	−14	5	0.821	116	7
Y	0.015	0.001	0.117	0.035	−19	3	0.914	90	−1
Yb	0.002	0.000	0.086	0.031	−19	4	0.852	70	6
Zn	—	—	—	—	—	—	—	—	—
Zr	0.322	0.05	0.057	0.051	−26	12	0.469	90	12

	(B) MT Vineyard								
	k (μg per 100 berries)		α (μg per 100 berries per day)		β (days from veraison)				
element	mean	SE	mean	SE	mean	SE	R^2	preveraison storage %	90% k
Ag	0.217	0.007	0.054	0.005	1	2	0.99	49	41
Al	68	5.74	0.057	0.015	−2	5	0.924	55	36
As	0.069	0.026	0.033	0.015	14	27	0.87	39	81

Table 2. Continued

| | (B) MT Vineyard | | | | | | | | |
| | k (μg per 100 berries) | | α (μg per 100 berries per day) | | β (days from veraison) | | | | |
element	mean	SE	mean	SE	mean	SE	R^2	preveraison storage %	90% k
B	844	0.044	0.048	0.005	8	3	0.988	45	54
Ba	71.55	1.44	0.098	0.019	−36	2	0.933	102	−13
Ca	42824	0.80	0.103	0.021	−37	2	0.931	102	−16
Cd	0.02	0.003	0.029	0.009	−4	13	0.927	55	71
Ce	0.172	0.009	0.098	0.025	−6	3	0.939	63	17
Cs	1.844	0.167	0.048	0.01	1	5	0.947	45	47
Cu	178	0.018	0.035	0.005	8	7	0.978	48	71
Dy	0.006	0.000	0.09	0.029	−10	4	0.897	63	15
Er	0.003	0.000	0.074	0.023	−8	5	0.891	64	22
Eu	0.007	0.000	0.077	0.016	−28	3	0.935	99	0
Fe	336	0.016	0.033	0.003	−5	4	0.99	62	62
Ga	0.018	0.001	0.071	0.018	−4	4	0.924	56	27
Gd	0.012	0.001	0.066	0.019	−6	5	0.903	67	28
Ge	0.007	0.001	0.037	0.018	−15	13	0.781	50	45
Hg	0.038	0.003	0.047	0.011	−5	6	0.933	61	41
Ho	0.001	0.000	0.062	0.026	−12	7	0.796	67	23
K	391235	14.90	0.053	0.005	2	2	0.988	50	43
La	0.078	0.004	0.083	0.021	−5	3	0.935	59	21
Li	0.113	0.004	0.06	0.006	3	2	0.988	47	40
Mg	21666	0.48	0.053	0.006	−27	2	0.98	82	14
Mn	219	0.004	0.081	0.015	−37	2	0.939	91	−9
Na	280	0.014	0.07	0.012	3	3	0.97	45	34
Nd	0.092	0.005	0.075	0.015	−3	3	0.955	59	26
P	35406	2.93	0.038	0.007	−4	6	0.962	63	55
Pr	0.021	0.001	0.076	0.016	−5	3	0.947	59	24
Rb	258.3	17.5	0.045	0.008	−4	4	0.962	52	45
Sb	0.026	0.002	0.047	0.006	13	4	0.982	42	60
Se	0.054	0.009	0.036	0.009	16	12	0.953	44	77
Sm	0.016	0.001	0.076	0.015	−6	3	0.953	59	23
Sn	0.635	0.047	0.061	0.017	−9	5	0.901	66	27
Sr	45.55	1.05	0.096	0.022	−36	2	0.916	105	−13
Th	0.044	0.002	0.082	0.016	−8	3	0.953	71	18
Tl	0.013	0.001	0.047	0.01	4	6	0.955	46	51
Tm	0.001	0.000	0.063	0.017	−12	5	0.897	68	23
U	0.003	0.000	0.056	0.012	−7	4	0.937	60	32
Y	0.021	0.001	0.093	0.029	−12	4	0.901	73	12
Yb	0.003	0.000	0.133	0.074	−10	5	0.805	102	6
Zn	76	0.005	0.042	0.019	−41	7	0.769	85	11
Zr	0.419	0.051	0.063	0.033	−15	9	0.704	92	20

[a] k = asymptote of the function; α = slope at origin; β = inflection point, expressed in days from veraison; R^2 = regression coefficients; preveraison storage % = percentage content accumulated until veraison as compared to the content measured on the last sampling date; 90% k = day on which the element reached an accumulation equal to 90% of k, expressed in days from veraison; SE = standard error; − = not calculated.

too late to effectively describe the starting phase of Ca accumulation (Figure 2a). A similar pattern was also observed for a few other elements (e.g., Ba, Mg, and Mn) in SM grapes but with R^2 values >0.7. Parameters of the logistic function for each element and vineyard are shown in Table 2. The nearly constant content of Zn and Tl always lower than the DL in SM samples meant it was not possible to include the data. The Cs, Rb, and Tl contents in the berries (as in leaves, data not shown) collected in one plot at the MT vineyard were considerably lower than those at the

other three plots, leading to the wide standard error bars shown in Figure 2. This can probably be explained by the higher content of exchangeable K found in the soil (data not shown) of this plot, which may have limited Rb and Cs uptake due to well-known antagonistic interactions.[15,31] Tl, commonly present in the ionic form M^{+1}, as happens for Rb and Cs,[14] could have a similar chemical behavior.

With a few exceptions, the accumulation patterns for a given element were quite similar in both vineyards, albeit with a different
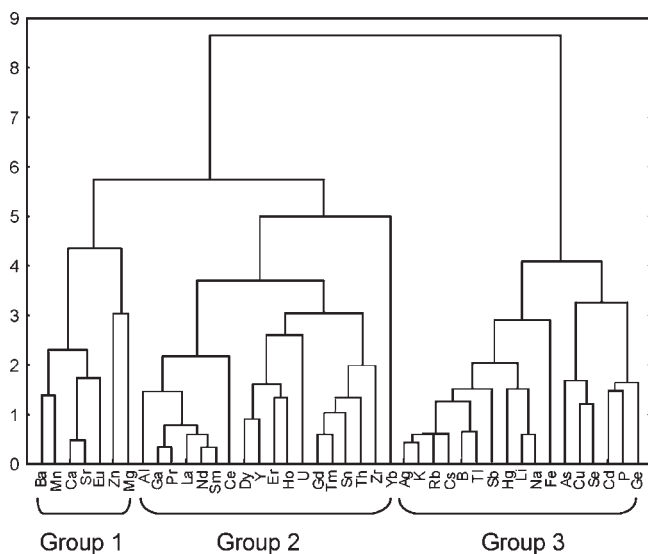
Figure 3. Cluster analysis (Euclidean distance, complete linkage) of the elements based on accumulation behavior during the development and ripening of the berry.

final concentration, probably related to the different availability of minerals, particularly trace elements, in the two soils.

Our results confirm previous observations[17] for Chardonnay berries, in which K content increased almost linearly during development and ripening, whereas Ca increased only up to 30—40 days after anthesis and then remained almost constant, confirming the role of this element in cell wall construction.[17] Similar results for K and Ca were also shown by different authors.[19,22,32] Other studies have shown Ca accumulation until ripeness.[20,30] For Mn we agree with Hradzina et al.,[32] who observed accumulation only during growth. For Na, different from other authors,[19,22,32] we observed a very clear accumulation pattern, with very similar content and curve shape in both vineyards. Our data for Mg on the SM vineyard were consistent with the observations of Esteban et al.[19] and Rogiers et al.,[22] with content increasing until harvest. In contrast, Mg in the MT vineyard showed an accumulation only during development, without changes during ripening, consistent with the observations of Hradzina et al.[32]

Cluster analysis applied to accumulation parameters (α, β, preveraison storage %, and 90% k) for the two vineyards permits the division of the 42 elements into three groups (Figure 3).

Group 1 included Ba, Ca, Eu, Mg, Mn, Sr, and Zn. These elements accumulate early during development, the amount being almost steady after veraison. As shown in Table 2, they are characterized by curves with early half accumulation times (low β value ranging from 28 to 60 days before veraison, Mg excluded) and a preveraison storage % per berry >71% of final content. With the exception of Ba, Mg, and Mn, even 90% k is early, often close to or prior to veraison. In this group, Mg and Zn showed particular characteristics, both having different accumulation patterns in the two vineyards.

Group 2 included Al, Ga, Sn, Th, U, Zr, and the rare earths analyzed, excluding Eu. These elements accumulate during both development and ripening but mainly prior to veraison. They are characterized by less early storage, with β between −26 and −2 days from veraison. At veraison, the content of each element was 55—116% of the final content, reaching 90% k by 36 days after veraison.

Group 3 included Ag, As, B, Cd, Cs, Cu, Fe, Ge, Hg, K, Li, Na, P, Rb, Sb, Se, and Tl. These elements increase progressively during the whole period investigated, reaching 34—64% of the final content around veraison, with β values of between −15 and 24 and 90% k between 28 and 116 days after veraison. In this group, As, Cd, Cu, Ge, P, and Se have an almost constant accumulation rate, reaching 90% k only 45 days postveraison or later.

In Shiraz grapes, the principal mineral elements were divided according to their accumulation pattern into two groups: those that accumulate mostly prior to veraison (Ca, Mn, and Zn) and those that accumulate throughout berry growth and ripening (B, Cu Fe, K, Mg, P, and S).[22] With regard to the common elements, we confirm this classification with the exception of Mg, for which we observed earlier accumulation.

Distribution of Mineral Elements in the Berry. On average, flesh, skin, and seeds represented 81.0, 15.2, and 3.8%, respectively, of the fresh weight of technologically ripe berries collected on the last five sampling dates.

Table 3 shows the average element content referred to 100 berries, determined in each part (skins, seeds, and flesh) for the SM and MT vineyards. The content of 33 of 42 elements in at least one of the three parts of the berry was significantly ($p < 0.001$) different for the two vineyards, probably because of the different soil characteristics.[23,24] In both vineyards, the differences between the last five sampling dates in terms of content of each element in the whole ripe berry, skin, and seeds were generally not statistically significant (Tukey's test, $p < 0.05$; data not shown). The very few differences observed were not systematic, showing no clear pattern, so we present and discuss only the results on mineral element distribution in the berry as a whole, without distinguishing between the sampling dates.

In both vineyards, the seeds were significantly the main sink for Ba, Ca, Mn, P, Sr, and Zn but lacked quantifiable amounts of Hg, Sn, Th, Tl, and Zr. The skin was the main sink for B, Ce, Dy, Ga, La, Nd, Pr, and Y, whereas the flesh was the main sink for Ag, Cs, Cu, Hg, K, Li, Mg, Na, Rb, Sb, Th, and Zr. Although not statistically significant, Ge content was higher in the flesh, whereas Al was higher in the skin. For some elements, significant differences were observed in only one vineyard. In the SM vineyard, Eu and Fe were higher in the seeds, whereas Se prevailed in the flesh and Gd in the skin. In the MT vineyard, Er, Ho, Sm, Sn, and Yb were higher in the skin, whereas As, Tl, and U were higher in the flesh. Tm was higher in the flesh in SM grapes but in the skin in MT grapes (Table 3).

The content of most elements in the berries was significantly different between the two vineyards, but the allocation percentage (as a geometric average) in the three berry parts was similar, with significant differences for only K and Li in all of the parts and for Ag, B, Fe, Mn, Rb, and Sb in the seeds, suggesting the existence of a common preferential sink. Indeed, when the mean content of the two vineyards is considered, highly significant differences (t test with $p < 0.001$) between the three parts exist for all elements (Table 4).

Our results confirm the higher Mg content in the flesh than in the skin and the berry localization of K and Ca found in other studies.[18,20,22] They are also largely in agreement with Rogiers et al.[22] with regard to P, Mn, Zn, and Cu in the Shiraz

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Table 3. Elemental Content (Mean of 400 Berries/Sample) in the Three Parts of the Berry, Taking into Account the Last Five Sampling Dates Corresponding to Technologically Ripe Grapes[a]

	UM	skin (sk)			seeds (sd)			flesh (fl)			SM vineyard			MT vineyard		
		SM	MT	sign	SM	MT	sign	SM	MT	sign	sk	sd	fl	sk	sd	fl
Ag	μg	0.049	0.069	***	0.025	0.024		0.090	0.101		b	c	a	b	c	a
Al	μg	26.2	31.5		1.23	1.84	***	22.1	29.1		a	b	a	a	b	a
As	μg	0.031	0.017	***	0.005	0.006		0.032	0.028		a	b	a	b	c	a
B	μg	240	366	***	39.9	51.1	***	167	286	***	a	c	b	a	c	b
Ba	μg	17.7	17.7		38.7	32.7		21.1	19.6		b	a	b	b	a	b
Ca	mg	9.64	7.66	***	26.7	24.7		11.5	10.0		b	a	b	b	a	b
Cd	μg	0.0038	0.0054	***	0.0029	0.0037		0.0032	0.0071					ab	b	a
Ce	μg	0.071	0.110	***	0.0017	0.0026		0.047	0.056		a	c	b	a	c	b
Cs	μg	0.015	0.461	***	0.003	0.135	***	0.024	1.011	***	b	c	a	b	c	a
Cu	μg	38.7	44.3		30.6	30.8		54.1	61.5		b	c	a	b	c	a
Dy	μg	0.0025	0.0039	***	0.0002	0.0003		0.0017	0.0020		a	c	b	a	c	b
Er	μg	0.0012	0.0020	***	0.0001	0.0002	***	0.0011	0.0011		a	b	a	a	c	b
Eu	μg	0.0021	0.0023		0.0029	0.0024		0.0019	0.0021		b	a	b			
Fe	μg	61.4	88.7	***	82.2	95.3	***	45.5	94.9	***	b	a	c			
Ga	μg	0.0078	0.0103		0.0005	0.0008	***	0.0045	0.0058		a	c	b	a	c	b
Gd	μg	0.0043	0.0063	***	0.0002	0.0003		0.0030	0.0052		a	c	b	a	b	a
Ge	μg	0.0019	0.0021		0.0008	0.0008		0.0029	0.0034		ab	b	a	a	b	a
Hg	μg	0.015	0.011	***	<DL	<DL		0.028	0.022	***	b	c	a	b	c	a
Ho	μg	0.0005	0.0008	***	0.00002	0.00002		0.0004	0.0004		a	b	a	a	c	b
K	mg	155	155		15.5	19.5	***	227	174	***	b	c	a	b	c	a
La	μg	0.031	0.045	***	0.0015	0.0018		0.019	0.028		a	c	b	a	c	b
Li	μg	0.042	0.028	***	0.002	0.002	***	0.164	0.071	***	b	c	a	b	c	a
Mg	mg	2.57	3.12	***	5.04	5.79	***	11.9	12.2		c	b	a	c	b	a
Mn	μg	49.8	61.5	***	95.6	98.1		36.9	62.5	***	b	a	c	b	a	b
Na	μg	39.5	37.2		10.7	12.0		195	210		b	c	a	b	c	a
Nd	μg	0.034	0.048	***	0.0016	0.0023	***	0.024	0.037		a	c	b	a	c	b
P	mg	6.83	8.10	***	13.0	13.3		8.08	8.86		b	a	b	b	a	b
Pr	μg	0.008	0.012	***	0.0002	0.0003		0.006	0.008		a	c	b	a	c	b
Rb	μg	16.1	71.9	***	3.42	21.49	***	29.0	136	***	b	c	a	b	c	a
Sb	μg	0.018	0.008	***	0.0091	0.0012	***	0.027	0.012	***	b	c	a	b	c	a
Se	μg	0.015	0.013		0.012	0.009	***	0.029	0.017		b	b	a	a	b	a
Sm	μg	0.0054	0.0083	***	0.0005	0.0006		0.0047	0.0067		a	b	a	a	c	b
Sn	μg	0.199	0.358	***	<DL	<DL		0.221	0.232		a	b	a	a	c	b
Sr	μg	28.4	14.6	***	44.8	20.8	***	19.9	9.38		b	a	c	b	a	c
Th	μg	0.009	0.010		<DL	<DL		0.029	0.032		b	c	a	b	c	a
Tl	μg	<DL	0.0024	***	<DL	<DL		<DL	0.008	***				b	b	a
Tm	μg	0.0003	0.0004	***	0.00002	0.00003		0.0004	0.0003		b	c	a	a	c	b
U	μg	0.0014	0.0012		0.0003	0.0004		0.0013	0.0018		a	b	a	b	c	a
Y	μg	0.009	0.014	***	0.0011	0.0013		0.005	0.005		a	c	b	a	c	b
Yb	μg	0.0011	0.0017	***	0.0001	0.0002		0.0012	0.0011		a	b	a	a	c	b
Zn	μg	18.9	20.8		40.4	40.9		5.12	12.28		b	a	c	b	a	c
Zr	μg	0.083	0.115		<DL	<DL		0.222	0.288		b	b	a	b	c	a

[a] SM = San Michele vineyard, $N = 20$; MT = Maso Togn vineyard, $N = 20$. t test ($p < 0.001$) and HSD Tukey's test ($p < 0.05$) significance (sign) are shown. Different letters indicate significantly different content. <DL = below detection limit; UM = unit of measurement.

cv., but with a higher accumulation of B in the skin than in the flesh and a higher Fe percentage in seeds. Higher B concentration in skin was previously shown,[25] confirming the role of this element in primary cell wall formation.[33] Furthermore, our results showed Mg localization in decreasing order in flesh, seeds, and skin, whereas Rogiers et al.[22] found a slightly higher percentage in seeds. We substantially confirm the preferential localization of rare earth elements in skin previously observed.[24,25]

Cluster analysis applied to the percentage distribution of elements in skin, seeds, and flesh divided the 42 elements into 3 groups (Figure 4). On the basis of the percentage content of the three parts (Table 4) it was possible to trace the groups back to their preferential distribution.

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Table 4. Elemental Percentage Distribution in the Three Parts of the Berry, Taking into Account the Last Five Sampling Dates Corresponding to Technologically Ripe Grapes[a]

	skin			seeds			flesh			SM + MT (mean)			
	SM	MT	sign	SM	MT	sign	SM	MT	sign	skin	seed	flesh	sign
Ag	30	36		15	12	***	55	52		32 b	13 c	55 a	***
Al	53	50		2	3		45	47		51 a	3 c	46 b	***
As	46	35		8	12		46	53		40 a	10 b	50 a	***
B	54	52		9	7	***	37	41		53 a	8 c	39 b	***
Ba	23	25		51	47		26	28		24 b	49 a	27 b	***
Ca	20	18		56	58		24	24		19 b	57 a	24 b	***
Cd	39	34		30	22		31	44		36 a	26 b	38 ab	*
Ce	60	63		1	2		39	35		62 a	1 c	37 b	***
Cs	36	29		6	9		58	62		32 b	7 c	61 a	***
Cu	31	32		25	23		44	45		32 b	24 c	44 a	***
Dy	56	61		5	4		39	35		59 a	5 c	36 b	***
Er	50	58		4	6		46	36		54 a	5 c	41 b	***
Eu	31	35		44	35		25	30		33 a	39 a	28 b	***
Fe	33	32		44	34	***	23	34		32 b	39 a	29 b	***
Ga	61	60		4	4		35	36		60 a	4 c	36 b	***
Gd	57	54		3	2		40	44		55 a	3 c	42 b	***
Ge	37	38		16	14		47	48		38 a	15 b	47 a	***
Hg	35	33		0	0		65	67		34 b	0 c	66 a	***
Ho	59	64		2	2		39	34		62 a	2 c	36 b	***
K	39	45	***	4	6	***	57	49	***	42 b	5 c	53 a	***
La	60	59		3	3		37	38		59 a	3 c	38 b	***
Li	20	27	***	1	2	***	79	71	***	24 b	2 c	74 a	***
Mg	13	15		26	27		61	58		14 c	27 b	59 a	***
Mn	27	28		53	44	***	20	28		28 b	48 a	24 c	***
Na	16	14		4	5		80	81		15 b	5 c	81 a	***
Nd	56	55		3	3		41	42		55 a	3 c	42 b	***
P	25	27		47	44		28	29		26 b	45 a	29 b	***
Pr	57	60		1	1		42	39		58 a	1 c	41 b	***
Rb	33	31		7	9	***	60	60		32 b	8 c	60 a	***
Sb	33	36		17	6	***	50	58		35 b	10 c	55 a	***
Se	26	35		22	22		52	43		30 b	22 c	48 a	***
Sm	51	53		5	4		44	43		52 a	4 c	44 b	***
Sn	46	59		0	0		54	41		53 a	0 c	47 b	***
Sr	31	33		48	47		21	20		32 b	47 a	21 c	***
Th	24	24		0	0		76	76		24 b	0 c	76 a	***
Tl	0	22		0	0		0	78		22 b [b]	0 c	78 a [b]	***
Tm	43	55		2	3		55	42		48 a	3 b	49 a	***
U	45	36		9	11		46	53		40 a	10 b	50 a	***
Y	60	65		7	6		33	29		62 a	6 c	32 b	***
Yb	45	59		5	5		50	36		51 a	5 c	44 b	***
Zn	28	28		63	56		9	16		28 b	59 a	13 c	***
Zr	27	28		0	0		73	72		28 b	0 c	72 a	***

[a] SM = San Michele vineyard, N = 20; MT = Maso Togn vineyard, N = 20; SM + MT = geometric means of the two vineyards, N = 40. t test ($p < 0.001$) and HSD Tukey's test ($p < 0.05$) significance (sign) are shown. Different letters indicate significantly different percentage content. DL = detection limit. [b] Considering only value > DL.

Group A includes Ba, Ca, Eu, Fe, Mn, P, Sr, and Zn. These elements accumulate mainly in the seeds (≥44% of total berry content, Eu and Fe in MT vineyard excluded).
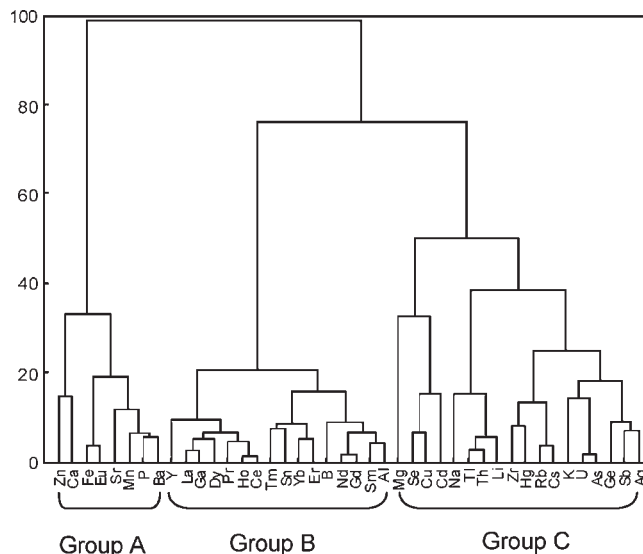
Figure 4. Cluster analysis (Euclidean distance, complete linkage) of the elements based on their distribution in the three parts of the berry.

Group B includes Al, B, Ga, Sn, and the rare earths analyzed, except for Eu. These elements accumulate mainly in the skin (≥43% of total berry content) and generally in small amounts in the seeds (<9%).

Group C includes the residual elements, Ag, As, Cd, Cs, Cu, Ge, Hg, K, Li, Mg, Na, Rb, Sb, Se, Th, Tl, U, and Zr. These elements accumulate mainly in the flesh (generally >50% and in some cases even >70%) and are present in the skin with content of <46% of the whole berry. In this group, Cd, Cu, Mg, and Se show relevant percentage content in seeds (>20%).

In conclusion, a summary and concise chart is proposed to highlight the three main types of behavior, taking into account both the accumulation and distribution pattern of elements in the berry (Figure 5): (1) accumulation before veraison and preferential sink in the seeds (Ca, Ba, Eu, Mn, Sr, and Zn); (2) accumulation above all before veraison and preferential sink in the skin (Al, Ga, Sn, and rare earth elements, Eu excluded); and (3) continuous accumulation throughout berry development and ripening and preferential sink in the flesh (Ag, As, B, Cd, Cs, Cu, Ge, Hg, K, Li, Na, Rb, Sb, Se, and Tl). A few other elements (B, Fe, Mg, P, Zr, Th, and U) cannot be unequivocally assigned to any of these groups.

The behavior of elements in the first group, which mainly accumulated in the seeds, could be explained, as previously suggested for Ca, Mn, and Zn,[22] on the basis of the low phloem mobility and discontinuity in xylem bundles of the outer part of the berry after veraison and berry enlargement.[20] We deem that this behavior could also be linked to early structural completion of seeds at veraison, so these elements would not be further moved into the ripening berry because they are no longer needed in the seeds. Ba, Eu, and Sr likely behave in a similar way to Ca, as they have similar chemical characteristics. The behavior of the elements in the second group, which mainly accumulated in the skin and are chemically characterized by a small ionic radius and a high oxidation state, could be explained by low mobility and a high affinity with plant cell walls, as suggested for rare earth element accumulation in wheat plants.[34] The behavior of the elements in the third group, mainly accumulating in the flesh,
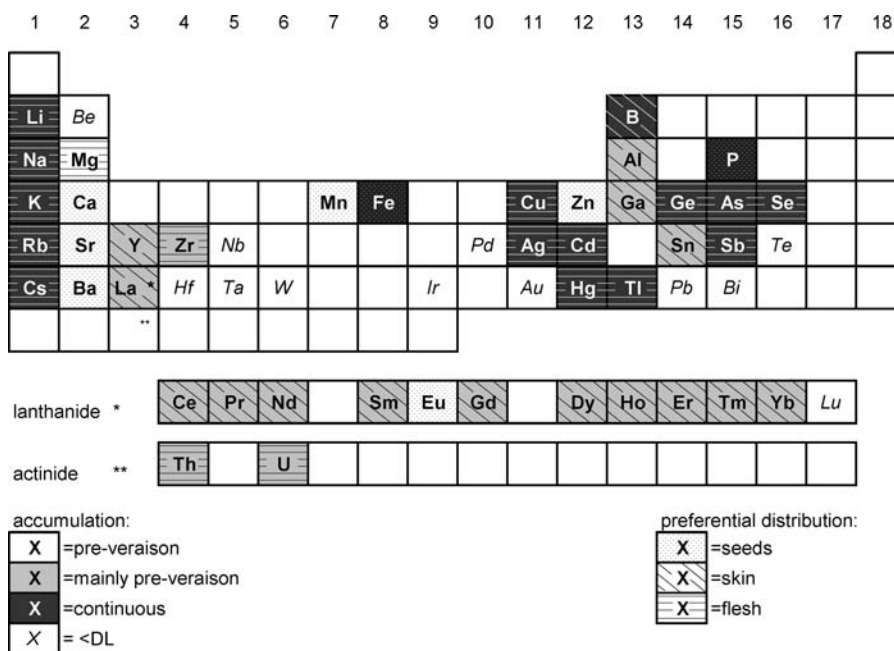
Figure 5. Accumulation and distribution pattern of the elements in the berry. <DL = below detection limit.

which is the part of the berry with the greatest storage capacity and volume, also growing during ripening, is in agreement with that of K and Cu observed by Rogiers et al.[22]

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DISCLOSURE

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ABBREVIATIONS USED

DL, detection limit; FW, fresh weight; ICP-MS, inductively coupled plasma—mass spectrometer; MT, Faedo-Maso Togn; NIST, National Institute of Standard and Technologies; SM, San Michele all'Adige.

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