Research Article

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A new statistical approach to the geochemical systematics of Italian alkaline igneous rocks

Abstract: The ultra-alkaline rocks have exotic features that frustrated many attempts to group them in a single classification diagram. A consistent classification would be very useful to define a possible consanguinity, an argument that feed a living debate. This paper investigates the petrologic characteristics of the Cenozoic Italian ultra-alkaline rock-suite using -Rank Entropy Anentropy (RHA) and Principal Component Analysis (PCA)-. The RHA formula is the succession of component's symbols arranged according to the diminishing of their elemental content in the analysis (whole rock composition). Other two parameters considered are an expression of the anentropy and entropy of the system. The PCA allows the definition of new latent variables based on geochemical compositions through linear combinations of the major oxides. Using both statistical methods was possible to create discrete groups of rock-types, associated by genetic relationship. The groups plotted in the Mg-Ca-Al ternary diagram depicts two main evolutionary arrays. We interpret the chemical variance in term of a general magmatic processes based on immiscibility and crystal fractionation. A comparison with similar association worldwide give a more general prospective to the magmato-tectonic assignment of these rocks, which is highly controversial in Italy.

Keywords: Classification, Alkaline and Ultra-alkaline, Italian magmatism, RHA method, Principal Component Analysis

1 Introduction

Italian magmatism appears to be among the most diversified and complex on the Earth, including rare rock-types such: kamafugites, carbonatites, melilitites, leucitites, lamproites and lamprophyres [1–4]. There is not a consistent classification based on modal features of lamproites, lamprophyres and kamafugites. Contrastingly, melilitites and leucitites modally classify in the QAPF system and derived diagrams. All these rock-types are ultra-alkaline rocks *sensu* [5] and are free or contain non-essential amounts of *plagioclase*. Therefore, in the diagrams used to classify basaltic rocks as TAS [6] or with R1-R2 [7] they fall into poorly defined fields or plot in chemical fields of rocks that are modally different, for example plagioclase-bearing rock-types, thus these classifications are misleading. In addition, when plotted in conventional diagrams, the ultra-alkaline rocks do not show a clear genetic correlation pattern. According to [8] the main features of ultra-alkaline rocks are an excess of alkalis relative to silica, this is reflected in an uncommon rock mineralogy. In particular, the excess of alkali can lead to the formation of alkali feldspars, both sodic and potassic feldspathoids, aegirine, sodic amphiboles and other phases rich in alkali but unstable in other magmas. For this reason the classification of ultra-alkaline rocks mainly uses, as discriminating criteria, the the presence of distinctive minerals (both on a modal and normative basis). Modal kalsilite discriminates kamafugites from melilite leucitites, normative larnite-discriminates melilitites from nephelinites (Ln Vs Ne [9]). Alkali ratio vs silica undersaturation discriminates kamafugites from lamproites rocks [10]. However, this methodological scheme does not allow a correct distinction of all ultra-alkaline rocks and often leads to a hybrid classification criteria, for example, with the recognition of particular mineralogical and geochemical features as in the case of lamproites [11] or particular mineralogical characteristics related to minor and rare minerals as in the case of lamprophyres [12]. Many of these accessory phases may derive from extreme differentiation processes that leads to formation of ultra-peralkaline residua able to concentrate specific elements in very rare mineral-phases and are rather representative of genetic processes than of a rock-type. Furthermore, as claimed by [13], while the knowledge of the mineralogical and geochemical characteristics of these rocks has improved since the beginning of the XX century, there are few papers designed to define

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the petrogenetic constraints of these. The absence of a single classification diagram for all ultra-alkaline rocks and the impossibility of a definite classification on a modal basis for lamproites and lamprophyres or in general for extrusive melilite-, kalsilite- and leucite-bearing rocks, suggests as opportune to consider the analyzed elements by means of statistical methods. In according with [13] and in general with IUGS also our goal is not to create a highly detailed taxonomy, impossible for the huge chemical variability intra and infra ultra-alkaline rock-types, but to provide a broadly based classification to be used in a logical manner by any geologist.

2 Distribution of Italian alkaline rock-types and geodynamic context

The Miocene to Recent tectonic structure of Italian area is characterized by the Apennine fold and thrust belt pulsing progression, and by net final extension balance leading to continental crust elision and formation of the Tyrrhenian basin. Most of the Italian alkaline magmatic activity strictly relates to the extensional phase [14]. The Paleogene magmatism mostly relate to limestone shelf Thetian foreland breaking. Figure 1 shows sampling sites and main tectonic domains, which influence the distribution of the different lithotypes. Even if the vast majority of the rocks which have been studied are associated with Plio-Quaternary active volcanic centers, older alkaline products reported in this work in peninsular Italy, are the lamprophyric rocks of Punta delle Pietre Nere (62-58 Ma) [15] and of Mount La Queglia (62-54 Ma) [14]. They took place during the subsidence of the Mesozoic carbonatic platform, an extensional phase that occurred in the Late Cretaceous-Paleocene [4, 16]. Similarly, the beginning of the alkaline activity in the Veneto Magmatic Province dates back to the Paleocene, but has substantial peak during the Middle Eocene [17–20]. Alkaline magmatic activity in the Veneto magmatic Province is essentially associated with intraplate extensional phenomena [18, 21–23].

In summary, at the origin of the Italian Neogene-Quaternary volcanic activity there is essentially the process of opening the Tyrrhenian basin, however the great variety of volcanic rocks erupted in the area, does not allow to define the tectonic process, which controlled the magmatic activity due to controversial interpretation of the rock-types. For several decades, many scientists have tried to propose possible models to correlate the geody-namic environment with a specific magma type. The most fashionable ones in the scientific world, also applied to the Italian magmatism although totally in contradiction to each other, are the rise of a mantle plume accompanied by lithospheric thinning [24–28]; the process of subduction with the formation of a back-arc basin (Tyrrhenian Sea) [29–32].

2.1 Analytical methods

The RHA method, as explained by [33], is a language of information [34, 35] which can be used to describe, group, organize and classify the composition of objects of any nature. Therefore, it's a simple and, at the same time, universal method to visualize the composition of any rock and to facilitate the creation of databases and the grouping of samples [36]. The method is essentially based on three parameters:

The first of the three parameters (**R**) - Rank formula – is the succession of the symbols of the components, deriving from a chemical analysis (succession of the symbols of the elements) or from a normative (or modal) analysis (succession of the symbols of the minerals), which are ordered according to the decrease in their concentration. In a system with 2 components, A and B, where the sum of the atomic numbers is 1 $(A + B = 1)$, we have the following sequences depending on the possible concentration values of A and B:

- If A > B => AB;
- If B > A => BA;
- If A = B = 0.5 => AB (In this case the alphabetical order is followed).

The same can be said about systems with 3, 4 or n components. In general, we tend to standardize and fix the number of components by stopping the Rank formula at a maximum of n=10 components [37]. For each set of parameters we will have a certain Rank formula, the order among different Rank formulas is not random but it's defined a priori through the choice of a specific sequence of components. If we have chemical components (*e.g.* chemical analysis of rocks), for each analysis we will have a certain Rank formula (**Rchem**) corresponding to a set of symbols, which are sorted according to the decrease in the atomic percentage [36]. In particular, Table 1 shows an example of recalculation of the Rank formula for Polino carbonatite [38]. As you can see from this example, with the RHA method all the elements that constitute the rock (oxides, volatiles and traces) are ordered by abundance, however, only the first 10 (the most abundant) must be used to classify the rocks. Several Rank formulas, each corresponding to a chemical
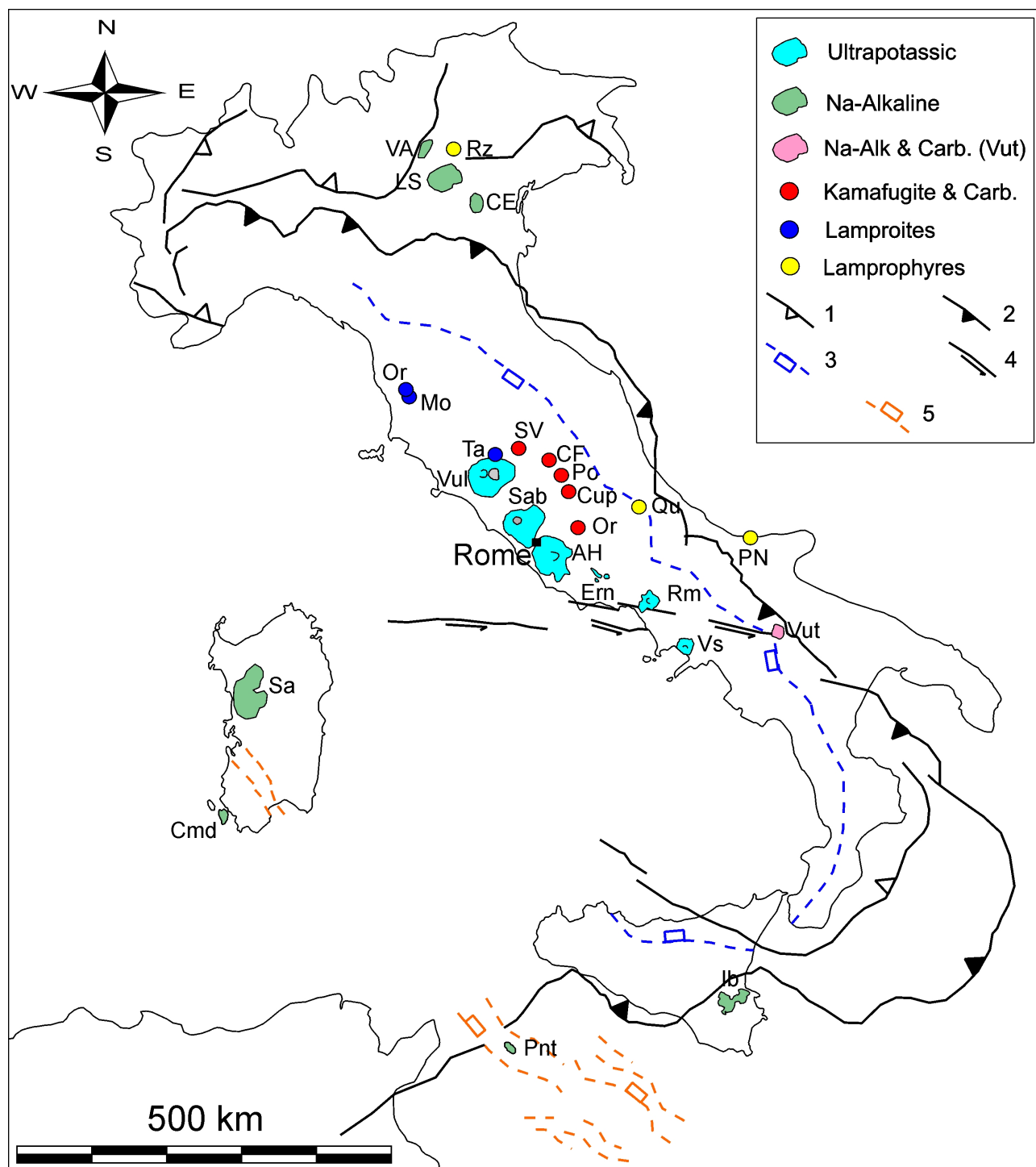
Figure 1: Simplified schematic map of distribution of alkaline and ultra-alkaline igneous center in Italy modify by [4]. VA=Val d'Adige (Vallagarina); Rz=Castelletto di Rozzo; Ls=Mt Lessini; CE=Euganean Hills; Or=Orciatico; Mo=Montecatini; Ta=Torre Alfina; SV=San Venanzo; CF=Colle Fabbri; Po=Polino; Cup=Cupaello; Or=Oricola; Vul=Vulsini District; Sab=Sabatini Districts; AH= Alban Hills; Ern=Mt Ernici; Rm=Roccamonfina volcano; VS=Mt Vesuvius; Qu=Mt La Queglia; Pn=Punta delle Pietre Nere; Vut=Mt Vulture; Sa=Sardinia (Melilogu e Marghine); Cmd=Sant'Antioco; Ib=Iblean Mountains; Pnt=Pantelleria; 1 Major Alpine thrusts; 2 Outer Quaternary front of the Apennine-Maghrebide thrust belt; 3 Outer Quaternary front of the intra-Apennine extensional belt; 4 Major transfer faults; 5 Sicily Channel rift system.

Table 1: Example of recalculation of the Rank formula (Rchem) for Polino carbonatite, the weight percent are converted atomic %, and the elements are arranged in order of decreasing atomic %. The symbol "=" between two elements shows that $p_i/p_{i+1} \leq$ 1,15, which corresponds to the difference between the neighbouring components not more than 15 relative percents

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	MnO	K_2O	Na_2O	P_2O_5	H_2O	CO_2
wt%	16.22	0.52	3.91	3.69	1.31	7.31	38.69	0.07	0.5	0.05	0.6	3.12	24.05
Rchem	O	Ca=	C	H	Si	Mg	Al	Fe	K	P	Ti	Na	Mn
At%	57	13.17	10.43	6.61	5.15	3.46	2.11	1.46	0.20	0.16	0.12	0.03	0.02

Table 2: Example of recalculation of entropy for Polino carbonatite, value of component (not in percent) are normalized at one (atomic portion/sum)

Component	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	H
$- p_i \ln p_i$	0.139	0.116	0.102	0.078	0.066	0.051	0.035	0.027	0.005	0.005	0.625

Table 3: Example of recalculation of anentropy for Polino carbonatite, where A = Aver * - ln (n)

Component	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	Aver.	A
$1/n \ln p_i$	0.243	0.880	0.981	1.179	1.287	1.460	1.675	1.834	2.693	2.792	1.502	0.502

analysis, will instead be hierarchically ordered on top of each other, on a vertical column, in accordance with the succession of the chemical elements in the Periodic Table. Sometimes different rocks can be characterized by the same Rank formula, in this case we use entropy and anentropy to distinguish them.

The second parameter (**H**) - Entropy, or rather, information on entropy is, essentially, a measure for the complexity of the system, typical of the uniform degree of the distribution of the components in a composition [39]. According to [40] the entropy of a composition, considered as a set of n values of the atomic quantity of the specific elements, is defined by [41, 42] as:

$$H = \sum (p_i \ln p_i) \quad \text{where } p_i \text{ is the atomic amount}$$
$$\text{of the component.}$$

H varies between 0 (when $p_i = 1$) and ln (n) (when $p_1 = p_2 = p_3 = \ldots = p_n = 1/n$). In order to normalize H between the interval 0-1, H is redefined as: $Hn = H / \ln (n)$, which is independent from the logarithmic base. In particular for the Polino carbonatite [38] the value of H is recalculation in Table 2, finally Hn (Entropy) = 0.625 ($Hn = H/\log_{10}10$)

If we consider a 3 components system: the entropy of the system has a maximum value when the 3 components are equal to each other; the minimum value when only one of the components is different from zero [40].

The third parameter (**A**) - Anentropy is a measure of "system purity". It's defined by [34] as:

$$A = -(1/n) \sum (\ln p_i) - \ln n.$$

Also the anentropy values vary from zero (when $p_1 = p_2 = p_3 = \ldots = p_n = 1/n$) to infinity (when $p_i = 0$ for at least an i element) [40]. To normalise A to the interval 0-1, the anentropy A should be divided into $A^{\#}$ - the anentropy of the «analytical absolutely pure system», in which $p_1 = 0.99955$, $p_2 = P_3 = \ldots = p_{10} = 0.00005$ [36]. In particular for the Polino carbonatite [38] the value of A is recalculation in Table 3, finally An (Anentropy) = 0.175 (An = A/ $A^{\#}$ where $A^{\#} = 2.871$).

If we consider a 3 components system, anentropy has a maximum value when only one component is different from zero, it has minimum value (0) when the three components are equal to each other. Like entropy, anentropy is also recalculated on the basis of the first 10 elements in the system to which the Rank formula refers [40].

The second methodology used for the study of the chemical analysis of Italian rocks is the Principal Component Analysis (PCA). The PCA (invented by Karl Pearson) is a statistical method (multivariate statistics), which, starting from a set of variables, has the purpose of creating a new set of minor variables so as to simplify the description of the system under examination. The initial variables, each of which is representative of a characteristic of the analyzed phenomenon, are converted into latent variables through a linear transformation. If we consider a matrix of quantitative data, such as that defined by the chemical analysis of rocks, with a size of **n** x **p**, we can transform the initial variables (defined in the matrix) into a new set of variables that are the main components. The new variables (**k**) will be: smaller than the previous ones **k** < **p**; linked to

Rank formula	En	An	Description
O Mg= Si Fe Al K Ca Cr Na Ni	0.538	0.256	peridotite_N2_Uganda
O Mg= Si Fe Ca Al K P= Na= Ti	0.546	0.222	peridotite mica_E.Aldan,Russia
O Si Na Al Fe K Ca Mn=Ti Zr	0.476	0.319	pantellerite_26_Pantelleria,Italy
O Si Na Al= Fe K Ca= Mn Ti Zr	0.476	0.321	pantellerite_34A_Pantelleria,Italy
O Si Na Al Fe K Ca Mn=Ti Zr	0.474	0.320	pantellerite_330_Pantelleria,Italy
O Si Mg Al K= Ca Fe Na Ti P	0.582	0.197	melilitite_It110_S.Venanzo,Italy
O Si Mg Al K Fe Ca Na Ti P	0.556	0.215	melilitite_It12_S.Venanzo,Italy
O Si Mg Al K= Fe= Ca Na=Ti P	0.553	0.220	kamafugite_CEL/7_S.Venanzo,Italy
O Si Al= Mg K= Ca Fe= Na P= Ti	0.566	0.175	lamproite_04GR05_R. of Macedonia
O Si Al= Mg K Ca Fe Na Ti P	0.555	0.192	tephrite Lct_It23_TorreAlfina,Italy
O Si Al Ca Mg K Fe Na Ti P	0.576	0.194	leucitite_SB-11_Sabatini,Italy
O Si Al= Ca Mg K Fe Na Ti P	0.576	0.194	leucitite_SB-15_Sabatini,Italy
O Si K= Al Mg Ca Fe Na Ti P	0.552	0.187	orendite_SIS-8_Corsica,France
O Si K= Al Mg Ca Fe Na Ti P	0.533	0.205	lamproite_SIS04_Corsica,France
O Si Ca Mg K Fe Al Ti P Mn	0.578	0.206	melilitite tuff_206.8_Belarus
O Si Ca Mg Fe= Al Na Ti P K	0.592	0.187	melilitite_13/4_Vulture,Italy
O Ca Si Mg Al Fe K P Ti Sr	0.559	0.250	carbonatite_PO2-5_Polino,Italy
O Ca Si Mg Al Fe K P Ti Sr	0.554	0.258	carbonatite_PO11B_Polino,Italy

Legend: Mantle | Pantellerites | High Mg | High Al | Lamproites | High Ca | Carbonatites

Figure 2: Show part of R, En and An calculated on a major element whole rock chemical analysis database of more than 2.000 data

the initial variables, as a linear combination of them; independent from each other (they are not related); sorted in decreasing function according to their variance.

By means of PCA we can define a new orthogonal reference system, through the linear transformation of the initial variables. This is because the main components are eigenvectors of the covariance matrix (it's a number that defines a measure of correlation degree among the variables), which is symmetrical. In particular, the component with the highest variance will be reported on the first axis (**x**) while the second component, which is determined according to its variance, will be reported on the second axis (**y**). The main purpose is to highlight the information present in this data and to reproduce it in the reference system which best represents its structure. In this way, if we analyze the main components (on the basis of variance) we'll reduce the complexity of the system. A peculiarity of PCA is that the transformation vectors of the variables are defined on the basis of the initial data itself. Or rather, both the coordinates of the new reference system and the rules to reduce the initial dimensions are defined in accordance to the properties of the covariance matrix or on the correlation matrix of the original data. Examples of linear transformations are rotation, reflection or homotheties. Therefore we can say that PCA consists in the rotation of the original data, compared to the reference system on which they are projected, the rotation is carried out in such a way that the first new axis is oriented in the direction of maximum variance of data, the second is perpendicular to the first and it's oriented in the direction of the next highest variance of data and so on for all new **d** axis [43].

3 Results

3.1 RHA method

Over 2000 analysis of alkaline and ultra-alkaline Italian and non-Italian rocks, was processed using the program Petros 3 [39]. RHA method associates each sample to a single Rank Formula, which will represent the new name of the rock due to its uniqueness (see supporting information 1 and 2). The analyzes used to build the database were chosen considering first the place of origin of the samples, many of which are holotype locality for these so rare rocks (*e.g.* Pantelleria for pantellerites). Therefore, only analyzes associated with rock samples were selected for which the authors of the publications (supporting information 2) had assigned a name consistent with the correct IUGS classification. Finally, the analyzes that showed total so far from 100 were discarded, while, to standardized the data, LOI is deleted. The anhydrous analyzes were reinserted into Petros 3 and recalculated at one hundred.

Considering the rocks characterized by similar Rank formulas, seven different classes were recognized (Figure 2). These are:

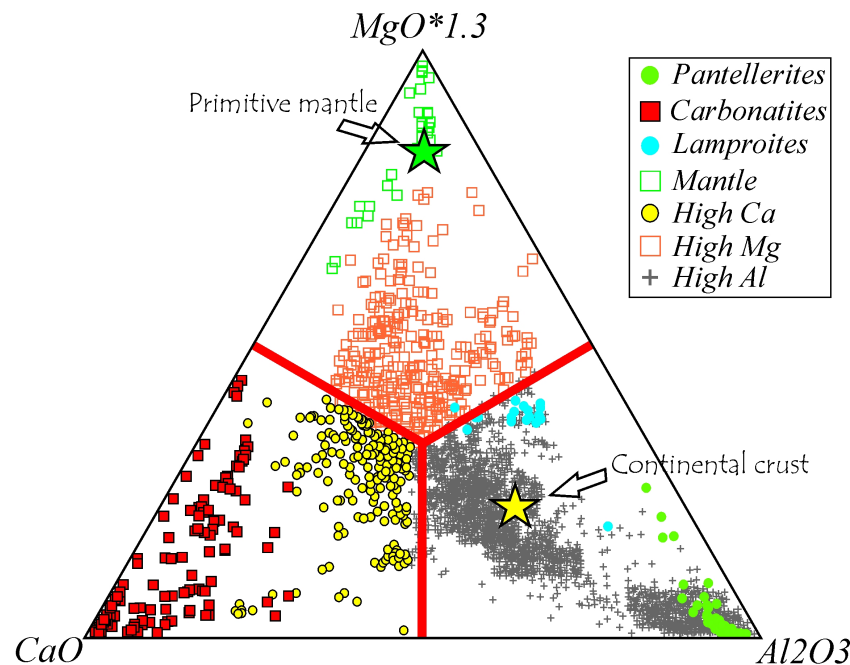**"Mantle"**, this class consists almost exclusively in kimberlites and peridotites;

Figure 3: Ternary diagram CaO-MgO*1.3-Al$_2$O$_3$ modify by [12]. the red half-lines define the statistical center of gravity of the triangle. The diagram shows the average compositions of primitive mantle and continental crust

"**Carbonatites**" this class is mainly made up of carbonatites and carbonatite tuffs;

"**Pantellerites**" this class substantially includes peralkaline rocks with high content of sodium (Na);

"**High Mg**" in this class many rock-types derive from mantle melts, in particular kamafugites, melilitites and ultramafic lamprophyres;

"**High Al**" this class is particularly large (more than half of Rchem, belong to this group). It is interesting to note that in this class are excluded (or present in negligible amount) rock-types such as: kimberlites, kamafugites, melilitites and carbonatites;

"**Lamproites**" this class is constituted only by 20 **Rchem** of only lamproitic rocks;

"**High Ca**", in this class unlike the class "**Carbonatites**", the calcium content is lower than that of silica, the most part of the rocks that belong to this group are kamafugites and melilitites.

The subdivision of the rocks that have been studied in these seven classes allows distinguishing all the examined rock-types and it shows, at the same time, a chemical separation, which is statistically relevant among carbonatites, kimberlites, lherzolites, kamafugites, melilitites and partially pantellerites, compared to the rest of examined rocktypes. As regards lamproites and lamprophyre, these are distributed in an undefined way among the various classes. In particular, lamproites are mainly distributed in three classes: "**High Mg**"; "**Lamproites**" and therefore, exclu-

sively in a sub-group of the "**High Al**" class. After having defined the classes, they found a method to represent the results graphically, therefore, all data, separated in the different defined classes, have been diagrammed again on TAS, R1-R2 and QAPF without obtaining clear distinctions.

Among the various diagrams that we have been used, the CaO-MgO*1.3-Al$_2$O$_3$ diagram, previously used by [12] for the distinction between ultramafic and alkaline lamprophyres, has allowed a better separation of the defined classes. The diagram has been slightly modified by increasing the MgO value by 13%. This measure aimed at improving the distinction among the "**High Mg**", "**High Ca**" and "**High Al**" classes, so that the data of the same were distributed appropriately, without exceeding the half-lines, which are defined according to the medians of the triangle and which join the center of the triangle with the sides of the triangle (Figure 3). In fact on this diagram, the different classes are all, or almost all, well discriminated, with the exception of the data included in the "**Lamproites**" and "**Pantellerites**" classes. These, even if they overlap with the data of the "**High Al**" class, form fairly defined groups. Moreover, considering the half-lines, which join the barycenter with the sides of the triangle, it is possible to distinguish at least three fields. Finally we compare data with the average values of the continental crust [44] and primitive mantle [45].

The seven different classes, define using Rank formula, are not apparent using entropy (**En**) and anentropy
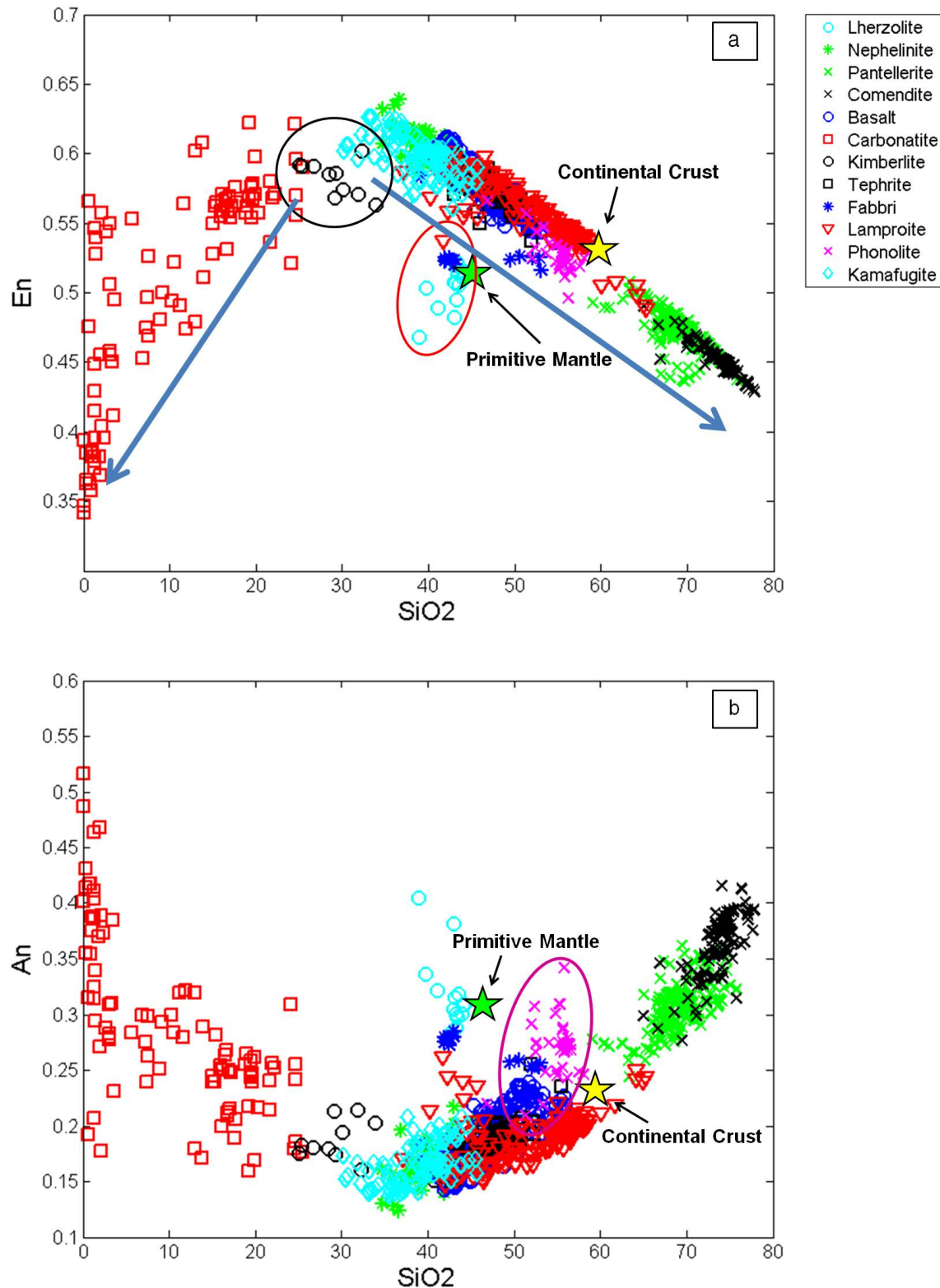
Figure 4: Binary diagrams - variation of entropy En (a) and anentropy An (b) in function of Silica. In figure a, the blue lines indicate the direction of evolution of the silicatic and carbonatic rocks, kimberlites are grouped by black circle, while red circle groups mantle peridotites. In figure b, magenta outline groups phonolites, which in this diagram deviate more from the trend of the other data

(**An**). However the feature of the two parameters is particularly evident when they are compared with well-known petrological indices. In particular, when the values of **En** and **An** were compared with the silica content (SiO$_2$ wt%) (Figure 4a and 4b). On this graphics, data were represented with different symbols and colors, in function of the different rock-types of origin. Use of the original nomenclature makes it easier to group the plotted data in addition to defining possible evolutionary trends, this is because either silica content and En or An not represents a distinctive character of the seven classes, defined starting exclusively from the Rank Formula. In fact, we observe that data arrange themselves in a very distinctive way. The trend of data is not accidental but links to the degree of evolution of the rocks. In particular, if we consider silicate rocks, on the diagram that is on the right of kimberlites, regardless of whether they have a mantle or crustal origin, we can see a decrease in **En** (or **An** growth) on the basis of the increase in silica content and the degree of evolution of the rocks (Figure 4a). For carbonatitic rocks, placed on Figure 4(a and b) on the left of the field occupied by kimberlites, the concept is similar, but opposite. In fact, in this case **En** grows (while **An** decreases) in a directly proportional manner to the increase in **SiO$_2$**. However in carbonatites, the degree of evolution decreases according to the silica content.

3.2 Principal Components Analysis (PCA)

Matlab has been used to elaborate a Principal Components Analysis (PCA) of the studied rocks. The first ten elements of the chemical analysis SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_{3t}$, MgO, CaO, MnO, K$_2$O, Na$_2$O and P$_2$O$_5$ was chosen as starting variables. This choice is due to the need to have initial variables with generally homogeneous quantities. Furthermore, in order to homogenize the values of original database, all the iron figures were converted into total trivalent iron. Then we applied PCA to the covariance matrix. The first results obtained with PCA were 10 new variables, the first three of them justify the 68.11% of variance. This initial value was increased by eliminating, carbonatites and many outliers, which were present, with cluster analyses. Then we proceeded with a new PCA that explains a variance explained by the first three components equal to about 86.74% of the total. The results obtained are shown in Figure 5, where besides the direction of variation of the major oxides and the values of continental crust and primitive mantle, we report the names of the rocks for all data and, therefore, for all analyses. Finally at the bottom right there is the histogram with the variance explained by the

different components, note that in this case the first five components explain a variance higher than 90%. For this diagram the principal two main components are defined as:

$$PC1 = ((SiO_2)(0.45)) + ((TiO_2)(-0.28))$$
$$+ ((Al_2O_3)(0.31)) + ((Fe_2O_3)(-0.25))$$
$$+ ((CaO)(-0.37)) + ((MgO)(-0.34)) + ((MnO)(-0.16))$$
$$+ ((K_2O)(0.28)) + ((Na_2O)(0.34)) + ((P_2O_5)(-0.3))$$

$$PC2 = ((SiO_2)(-0.19)) + ((TiO_2)(-0.5))$$
$$+ ((Al_2O_3)(-0.24)) + ((Fe_2O_3)(-0.55))$$
$$+ ((CaO)(0.40)) + ((MgO)(-0.25)) + ((MnO)(0.28))$$
$$+ ((K_2O)(0.06)) + ((Na_2O)(-0.19)) + ((P_2O_5)(-0.13))$$

At this point, if we consider these components (or better the coefficients of the components) as the best ones, because they explain the maximum variance, we re-inserted the eliminated data by recalculating them according to the coefficients of the last defined components (Figure 6). On the last PCA we can identify a distinction for the projected rocks both on a genetic and evolutionary basis. In particular, along the PC1, mostly influenced by the silica content, there is a genetic distinction between rocks, which probably have a mantellic origin, and rocks which probably have a crustal origin, the zero of PC1 represent the compositional limit between mantle and crust. Along the PC2 there is a chemical difference between rocks that evolve towards terms rich in sodium and rocks that evolve towards terms rich in potassium, in this case the zero of the PC2 represents the limit between the two evolutionary phenomena. In fact, according to a detailed analysis of the diagram, we can notice a clear distinction among felsic rocks, that fall in the eastern quadrants of the diagram and they get rich with sodium. The data concerning mafic and ultramafic rocks tend to concentrate in the western quadrants, in particular basalts, nephelinites, haüynophyres in the south-western quadrant, while lamproites, leucitites and phonotephites in the north-western one. The distinction among the different rock-types is more highlighted if we consider a 3rd component, besides the two main ones we can start to distinguish different groups of rocks. In particular, by rotating diagram with three components (Figure 7a and 7b), we can clearly distinguish 8 different rock-types (phonotephries, haüynophyres, kimberlites, comendite, pantellerite, phonolite, rhyolite and lherzolite). Therefore, the PCA than the Rank method shows a best correlation with the IUGS nomenclature used for these rocks, but still unable to distinguish all the lithotypes investigated.
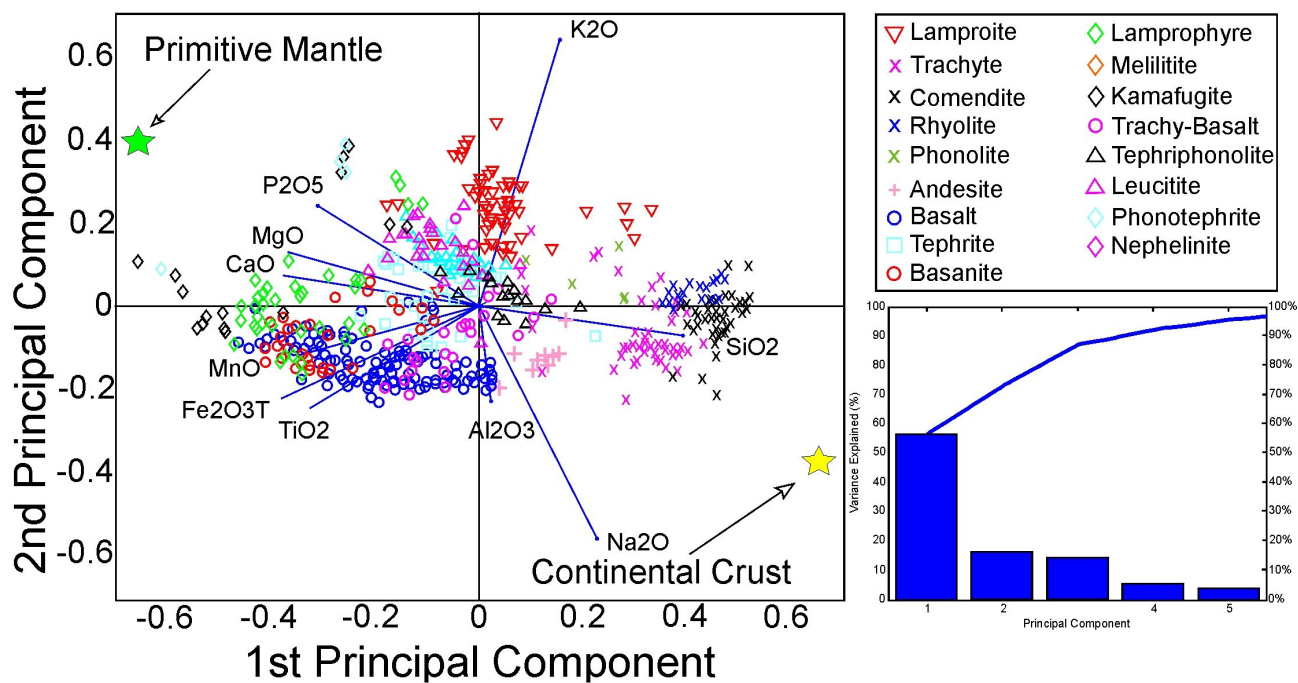
Figure 5: Principal Component Analysis, on the horizontal axis the 1st component (PC1) by variance is reported, while on the vertical axis the 2nd one (PC2). The stars are average values of primitive mantle and continental crust recalculated according to the first and second main components. At the bottom there is the frequency histogram with the variance explained by the different components.
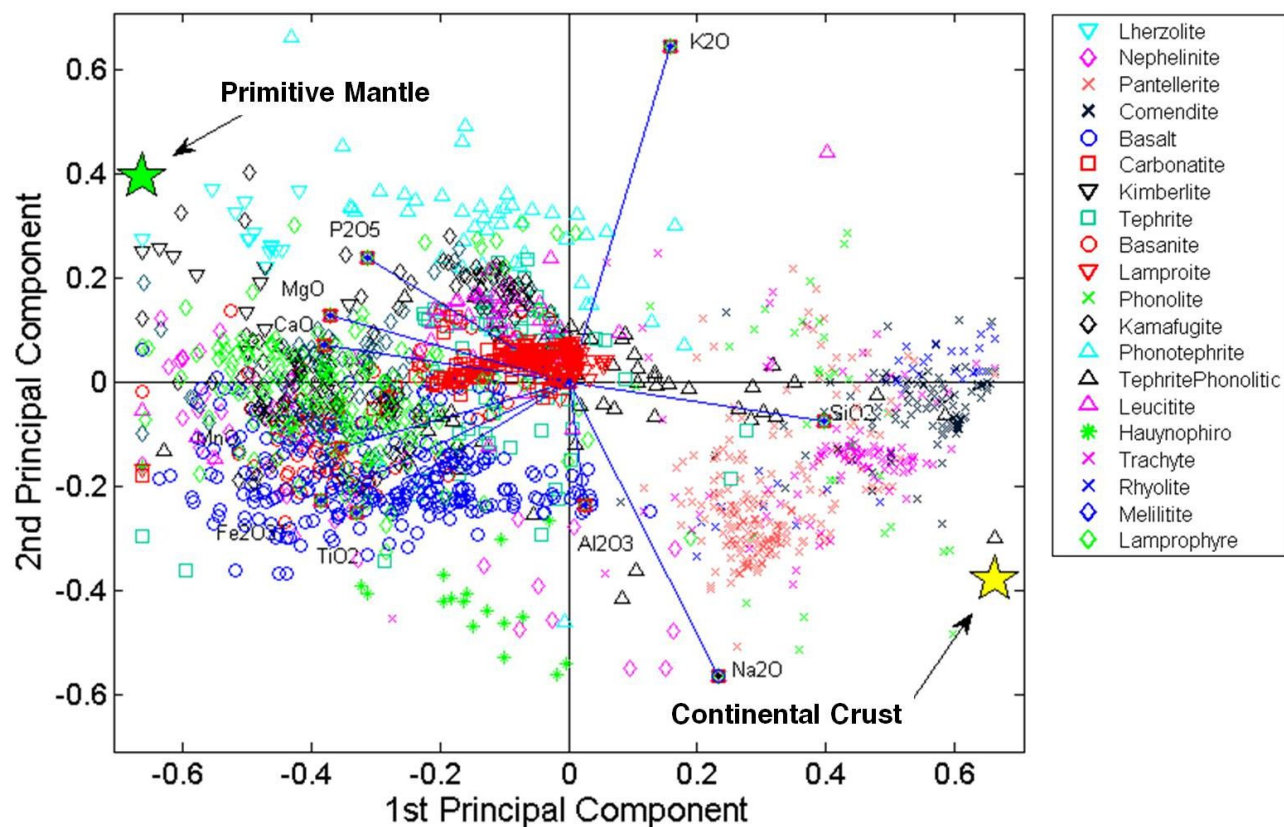

Figure 6: Principal Component Analysis, on this diagram the outlier are recalculating to the coefficients of the best components.
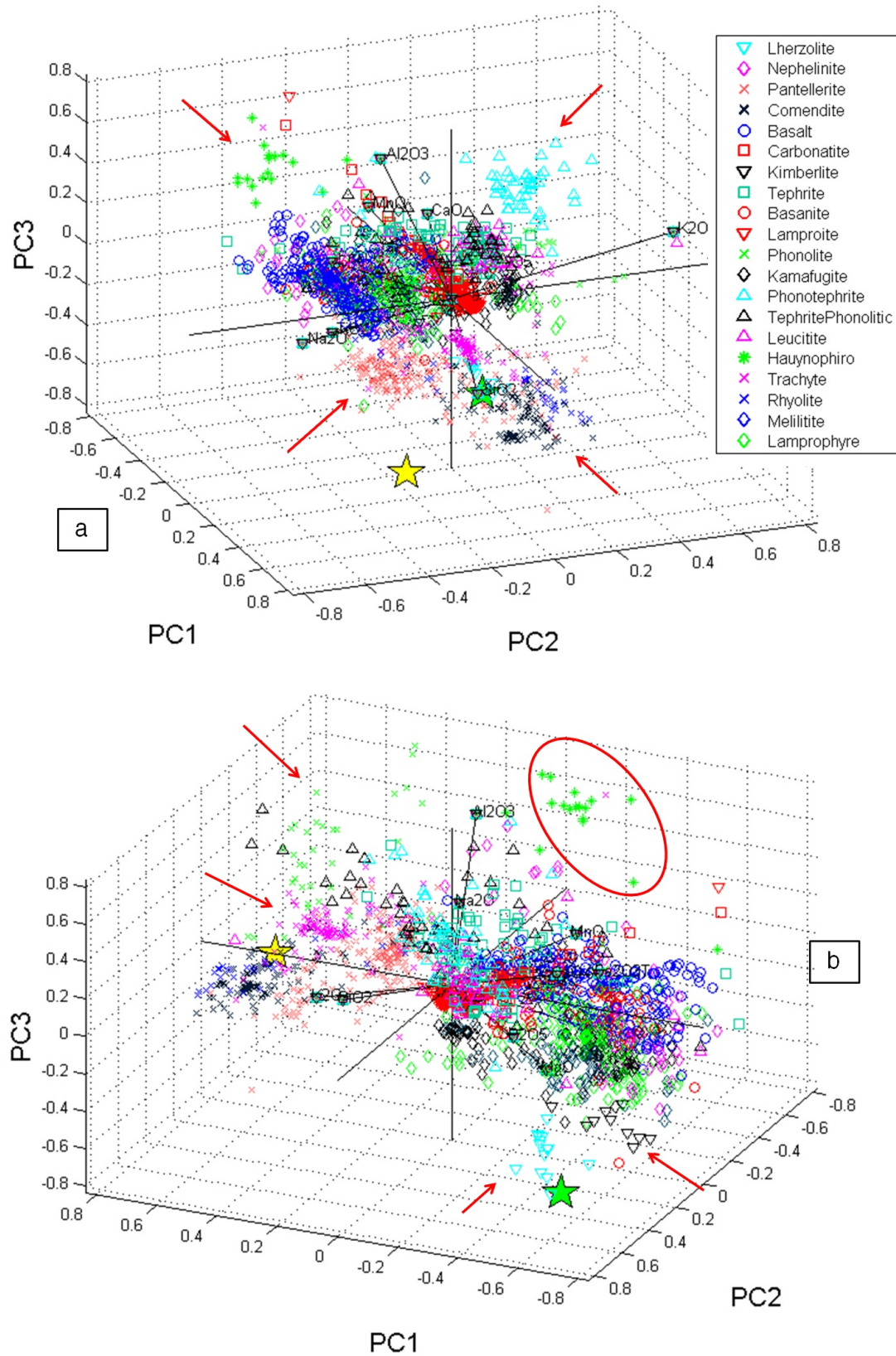
Figure 7: Three component diagram of Principal Component Analysis (PC1, PC2 e PC3) by rotating diagram we can clearly distinguish different rock-types.

However, potentially, since the method substantially bases on the definition of 10 main components, by varying the combination of these components it is theoretically possible to distinguish all the rocks projected on the diagram. Finally the greatest evidence obtained using the PCA is, as for the Rank formula, the distinction of the lithotypes in groups characterized by a common genetic origin.

4 Discussions

The statistical methods highlight the main characteristics of ultra-alkaline rocks giving a general picture of their chemical distribution. Furthermore, regardless of the chosen method, the result does not seem to be influenced by the age of the rocks studied. In fact, even if most of them have a Cenozoic age, in the dataset ancient lithotypes are included such as: Early Cretaceous alkaline lamprophyres of Southern Tuscany [46] or as Late Paleozoic Pantellerites and comendites of Southern Mongolia [47]. Too many different rock-types makes it difficult to define discrete homogeneous classes for all investigated rocks. In particular, lamproites and lamprophyre distribute with RHA method among various classes. This particular behavior is due primarily to the conditional choice of classifying these rocks, rich in hydrated phases, on dry base due to the paucity of chemical analyses having volatile species (OH, F, Cl, S) determined. Moreover, lamproites and lamprophyres groups compared to other ultra-alkaline rocks shown, within the same group, a larger chemical and mineralogical heterogeneity. Rank Formulas were used for the definition of different classes of rocks. Lamproites and the lamprophyres tended to form small groups characterized by similar Rank Formulas and similar values of entropy and anentropy. In particular, as regards the chemical analyses of the rocks of Orciatico, Montecatini Val di Cecina and Torre Alfina (a lamproitic affinity rocks [48]) these showed the same Rchem, forming, within the "High Al" class, a single clear chemical cluster.

RHA method allowed, using Rchem, a general distinction of the studied rocks, in terms of large classes, which are similar from a chemical point of view. This distinction in classes characterized by same or similar Rank formula represents an innovation in the use of the RHA method with respect to past works (*e.g.* [36]), as well as their graphic representation (Figure 3). In particular, the method allows to distinguish the examined rock-types, kalsilitites and melilitites, (which substantially belong to the **"High Mg"** and **"High Ca"** classes) from the rocks of the Roman Province (which mainly belong to the **"High

Al"** class), confirming the classification diagram proposed by [49]. Moreover when we compared the data with crustal and mantel value, we can see that previous classes are likely genetically associated. In particular, in the Figure 3 we can see that all the rocks, which fall at the top of the triangle, are somehow related to the mantle. Those that fall in the lower right field are genetically associated with the crust and, finally, those that fall into the lower left field are plausibly related to the carbonatites. These 3 main groups of rocks regardless of the method used: mantle-derived rock, crustal-derived rocks and/or linked to other genetic processes and, finally, carbonatitic rocks; are always graphical different, regardless of the chosen method. In fact as regards the Principal Components Analysis (PCA), it's possible to distinguished rocks with mantellic origin and rocks with crustal origin just using the first component. A further feature of PCA is that data on the two main components, as on the TAS, are simple to interpret from a graphical point of view. In general, regardless of the method used, the statistical approach shows the possibility of comparing alakline and ultra-alkaline rocks on a unique diagrams (Figure 3 or Figure 7). Indeed, on TAS [6] and R1-R2 [7] (Figure 8) the data are overllapped in a caotich and confused manner, falling into statistically undefined fields or worse on classification fields typical of other rocks. However it must be specified that the particular distribution and correlation of the geochemical data on the diagrams of Figure 3 and Figure 7, are partially related to the constant sum problem [50]. Although several papers have been published in which the authors have tried to minimize this effect [51–53], no general solution to the problem has been found. In fact, this problem affects all the most common bivariate and multivariate diagrams based on geochemical data including the TAS and the R1-R2, which are used to compare the results of my work.

Entropy and anentropy are basically two parameters, which provide qualitative and non-quantitative information. The greater or lesser complexity or purity of the system, in the case of rocks, depends fundamentally on the chemical composition of the same. This is reflected in a minor or greater mineralogical complexity. In fact, rocks consisting of a few mineral species, one of which is clearly more abundant than the others, will be characterized by high values of anentropy-purity (**An**) and by lower values of entropy-complexity (**En**).

In the light of the above, the "anomalous" values of En and An in Mantle and Colle Fabbri (grouped with black and red outlines on the Figure 4 a) are caused by a limited chemical and mineralogical variance of the same. In fact, En, An and SiO_2 content, in this rocks are limited to its stoichiometric composition (mineral chemistry), be-
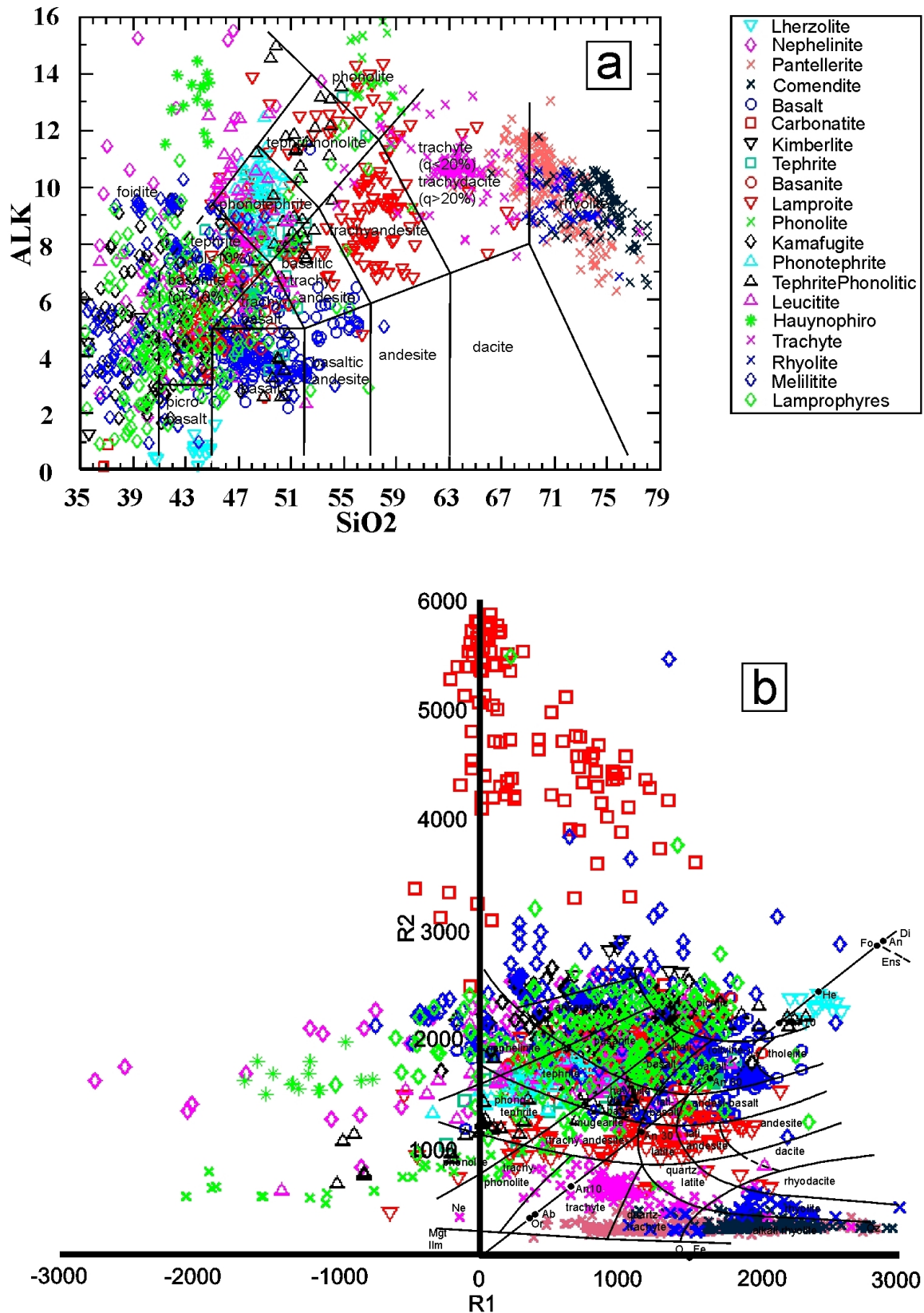
Figure 8: Distribution of alkaline and ultra-alkaline rock data on Total Alkali Vs Silica (a) and de La Roche (b) classification diagram.

cause mantle minerals are statistically invariant. Colle Fabbri, is also associated to the little mineralogical variance of these rocks, which are substantially almost monomineralic (melilitolite). Finally as regards the particular trend of phonolites on the SiO_2 vs **An** diagram (grouped with a magenta outline Figure 4 b) this can be associated with the high alkali content in these rocks, which is more evident in a change in the value of **An**. That is because **An** is strongly influenced by the variation in the minor components [33].

On Figure 4 diagram it is possible to distinguish 3 main groups of rocks: carbonatitic rocks; mafic rocks; felsic rocks. Furthermore, on this diagram we can postulate a possible genetic hypothesis about the examined rocks by considering the binary diagrams SiO_2 Vs **En** and SiO_2 Vs **An**. In fact, for both carbonatic, mafic and felsic rocks, the values of En and **An** decrease or grow according to the evolutionary degree of the rock. In general, more the rock is evolved, more it is, from a statistical point of view, chemically "pure". Because substantially consists of a few elements but in large quantities (silica for mafic and felsic rocks, calcium for carbonatitic). Finally, looking at these two figures the last consideration we can make, is to consider kimberlites as less evolved rocks (grouped with a black outline in Figure 4a) and they divide (KIMBERLITE DIVIDE or kimberlitic limit) the two different evolutionary trends. We must specify that in kimberlites rocks the lower values of complexity (or greater of purity) are linked to the abundant contamination of xenoliths and xenocrystals mantle.

On this diagram it is not hazardous to hypothesize a common origin for carbonatitic and mafic rocks, linked to the partial melting of the mantle, which leads to the formation of a melt with values of silica and entropy similar to those of kimberlites (so, substantially with a lower silica content and a greater entropy, if compared to the mantle). A carbonatitic and a silicatic liquid are separated from this melt by immiscibility, which evolve in opposite directions.

Finally, felsic rocks are linked to a different petrogenetic process which, however, does not influence this evolutionary trend.

Although rock classification represent only the initial stage for develop a hypothetical genetic model, in our case it is the only solution able to represent a big dataset with Italian and worldwide alkaline and ultra-alkaline rocks of different ages. In fact, the model highlights only the common genetic process at the origin of ultra-alkaline rocks, while, due to the multiple magmatic sources of the studied rocks, it is impossible to define cognate lines of the different parental magmas. Logically on single volcanic districts or also magmatic province, are indispensable in the development of a consistent petrogenetic model detailed infor-

mation of: isotopic ratios, mineral chemistry and trace element composition (*e.g.* [54, 55]).

5 Conclusion

1. The RHA method is a statistical approach for rock classification, based on the concept of order (An) - disorder (En), which is reflected in the greater or lesser mineralogical complexity of the rocks and, consequently, on the degree of evolution of the same rocks. Consistent rock-type groups are then identified on a statistical base: carbonatites (RHA's class Carbonatites), pantellerites (RHA's class Pantellerites), kimberlites (RHA's class Mantle rocks) and, partially, a small group of lamproites (RHA's class Lamproites). The other 3 classes defined are more heterogeneous and consisting predominantly by: kamafugites, melilitites and ultramafic lamproites (High Mg class); tuff carbonatititic rocks, kamafugites and melilitites (HighCa class); finally HighAl with foiditic rocks, alkali basalts and peralkaline rhyolites, but with negligible amount of kimberlites, kamafugites, melilitites and carbonatites.

2. Ternary diagram CaO-MgO*1.3-Al_2O_3 modified after [12] defines classes clearly separated from each other, which form to distinctive genetic lineage; the separated classes do not show links with the entropy and anentropy parameters; Entropy and Anentropy are always well correlated when compared, individually, against the common petrological indices, highlighting clear links with the evolutionary degree of the rocks. In particular this diagram show: a petrogenetic process, which leads to diverge the rocks with carbonate from those without carbonate on two specular trends originated by immiscibility and crystal fractionation, that have a single origin in the mantle; a third group (consist by more evolved silicatic rocks) clearly denounces a different source that seems to be related to the continental crust, but could also belong to a type of mantle or magmatogenetic phenomenon not yet well understood.

3. On the principal components analysis (PCA) allows, graphically a distinction of the rocks on a evolutionary basis along the 2nd component by variance (PC2), where the zero divides, chemically, the rocks that differ, enriching themselves in sodium, from those that evolve enriching in potassium. The zero of the 1st component (PC1) defines two different genetic processes, dividing the mantle-derived rocks from those

of crustal derivation (or linked to the crust by a different process). Finally, the method allows to distinguish 8 types of rocks (phonotephries, haüynophyres, kimberlites, comendite, pantellerite, phonolite, rhyolite and lherzolite).

4. Statistical classification of alkaline and ultra-alkaline rocks: did not allow clear discrimination from the taxonomic point of view, due to the particular chemical mimicry that these rocks show in opposition to their modal allomorphism, or rather that their mineralogy is unique and peculiar only of them, although exotic; the chemical schemes applicable to other rocks that are disappointing in describing the virtual and material factors, which determine this peculiarity, among these, mainly, the role of carbonates and volatiles. It is possible to follow a non-taxonomic way, but genetics for the classification of these rocks, which cannot be pigeonholed into distinct lithotypes, but rather, they form genetic clans in which apparently different rocks are related to a single petrogenetic logic; paradoxically, the simpler the classification scheme the more efficient is, although it does not allow us to give a specific name to each rock and, therefore, we must consider that the IUGS nomenclature can be maintained; the intuition of Rock that these rocks can be considered clans within different tribes corresponds.

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