

Elemental Variation and Petrogenesis of Pyroxenes in HED Meteorites By Multivariable Discriminant Analysis Method. Z.X.

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Introduction: HED (howardite, eucrite and diogenite) are meteorites with mafic and ultramafic igneous composition. Previous studies suggested HED came from asteroid (4) Vesta and they were generated by magmatic melting followed by differentiation crystallization, metamorphic, and impact [1,2,3,4,5]. Uniform oxygen isotopic composition of HED samples favors global magma ocean for (4) Vesta [6, 7]. However, the petrological diversity of HED may indicate more complex magma processes in the meteorites. In general, most of the geochemical studies are using traditional methods (e.g. element to element or ratio to ratio plots) to classify the different rock type and groups. With the traditional methods, only limited elements can be show in a figure. As such, some meteorites may have been identified as HED by a traditional method but found different either in isotopic composition or other elemental characteristic. These anomalous HED meteorites may or may not come from asteroid (4) Vesta. In fact, magma is a unit system where any elemental change should affect to all other elements as a whole, it would be reasonable to consider all elements together to look for the systematical changes. Using multivariable discriminant analysis (MDA) method is one of such testing for their geochemical variation. The method may be able to help us to better understand the petrologic processes and the relationship among elements. This study is to test the MDA method by focus mainly on pyroxene composition of eucrite and diogenite.

Method. The MDA is a statistical technique for studying difference between two or more groups with multiple variables simultaneously [8, 9]. MDA method tries to derive a set of canonical discriminant functions, which is a dependent variable that has weighted linear relationship with multiple independent variables. The weight is call discriminant coefficients. The function can be expresses as $f_{km} = u_0 + u_1 X_{1km} + u_2 X_{2km} + \dots + u_p X_{pkm} + \epsilon_j$ (where f_{km} is the canonical function for case m in group k, and $X_{1km}, X_{2km}, \dots, X_{pkm}$ are the independent variables; ϵ_j is the error and the u_0, u_1, \dots, u_p are discriminant coefficients). All data in this study have been standardized by z-score method. The z-score indicates how many standard deviations that an element x away from its mean \bar{x} . $z\text{-score} = (x - \bar{x})/\sigma$ (where x is an element in the variable; \bar{x} is the mean of the variables and σ is the standard deviation). The correlations between elements have been checked to see if any elemental correlation could be evaluated. The data set has included more that 200 pyroxenes samples; each has 9 major element oxides. All elements were analyzed by geochemical instruments independently by different research groups and combined together by Mittlefehldt [1]. SPSS (Standard Version 11.5 for Window software, SPSS Inc), a professional statistic program, is used to analysis these data. Detail method can be referred to [10] and [11] as well.

Initial Results. Figure 1 is the canonical discriminant Function diagram for the pyroxene data of eucrites and diogenites. The canonical discriminant functions are generated by multivariable analysis program in SPSS. X-axis is for function 1 defined by z-score of nine elements and Y-axis is for function 2. Function 1 has the largest differences between groups and Function 2 is orthogonal to the first function as the second largest among the functions. Each element in the function has a coefficient that generated by MDA analysis.

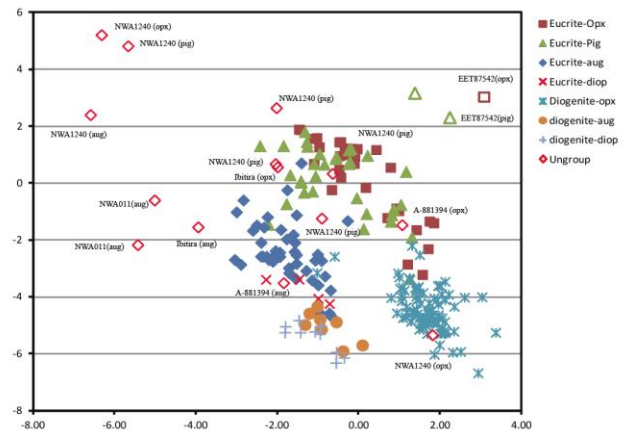


Figure 1. The Canonical Discriminant Function diagram for the pyroxene data of eucrites and diogenites in this study. X-axial is for Function 1 defined by Z-score of nine elements and Y-axial is for Function 2. Z-score is the number that derided from value of the variable different then there group average and divided by their standard divination. Opx=orthopyroxene, aug=augite, diop=diopside, Pig=pigeonite.

Two main groups show up in the diagram before we bring in their mineral phases. The two groups do not separate by eucrites and diogenites but by their mineral phases. When mineral phases of the samples bring into consideration, diogenites can be classified into two subgroups, one is orthopyroxene; the other is augite and diopside. For eucrites, the orthopyroxene and pigeonite groups are also separate from augite and diopside groups. Both groups in eucrites with one end of the field overlapped with groups in diogenites. In general, the mineral phase show limit variation in its own groups within their rock types.

Table 1 shows coefficients of elements calculated for canonical discriminant function. The coefficient shows the contribution of the variable to the change of the function. Thus, the percentage of a coefficient to the total can reflect the impact of the variable to the functions of 1 and 2. The impact value is then calculated by the absolute value of the coefficients for F1 plus that for F2

than divided by total of all coefficients. The slope is the ratio of coefficients of the element, thus for the coefficient in F2 divided by that in F1. The coefficients of the functions can be used to estimate the impact of individual element to the classification.

Structure Matrix			Impact factor	Slope
Function	1	2	%	F2/F1
Zscore(SiO ₂)	0.682	-0.731	18.91	-1.07
Zscore(MnO)	0.513	0.859	18.36	1.67
Zscore(MgO)	0.538	-0.525	14.22	-0.98
Zscore(FeO)	-0.652	0.363	13.58	-0.56
Zscore(Cr ₂ O ₃)	0.351	0.515	11.59	1.47
Zscore(NA ₂ O)	-0.458	0.181	8.55	-0.40
Zscore(CaO)	0.103	0.376	6.41	3.65
Zscore(Al ₂ O ₃)	0.128	0.215	4.59	1.68
Zscore(TiO ₂)	-0.215	0.068	3.79	-0.32

Table 1. The impact value indicates how much the element change could affect the variation of functions; and the slope will show the direction of the variation.

In this study, SiO₂, MnO, MgO, FeO and Cr₂O₃ have impact value larger than 11%. These values may explain why SiO₂, MnO, MgO, FeO and Cr₂O₃ are selected in most the element to element diagrams in previous studies. The slopes for these elements indicate SiO₂, MgO, and FeO are negative, but MnO, CaO, Cr₂O₃ and Al₂O₃ are positive. The slope of positive in Figure 1 shows the mineral phase change from orthopyroxene to clinopyroxene. Slope for SiO₂, MgO and FeO is negative that is along the change from diogenite to eucrite but maintain the same mineral phases in pyroxene. The slope of elements change may reflect different magma processes only in simple mineral composition are used in MDA analysis; it may not be the same in traditional element to element method.

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO
SiO ₂	1.00							
TiO ₂	-0.36	1.00						
Al ₂ O ₃	-0.13	0.18	1.00					
Cr ₂ O ₃	-0.08	-0.07	0.55	1.00				
FeO	-0.80	0.24	-0.14	-0.07	1.00			
MnO	-0.21	-0.11	-0.02	0.23	0.32	1.00		
MgO	0.77	-0.36	0.18	0.23	-0.72	-0.12	1.00	
CaO	0.28	0.05	-0.07	-0.22	-0.59	-0.35	-0.12	1.00

Table 2. Correlation between elements in z-score

The elemental correlation calculated by the MDA program is also an important index geochemical relationship of element within minerals. One set of the elements (SiO₂, MgO, FeO) shows strong correlation (0.77 to 0.80 when 1.0 is the maximum) and two sets of elements (FeO, CaO) and (Cr₂O₃, Al₂O₃) have correlation more than 0.55. Correlation between

SiO₂, MgO, and FeO can be explained by forming base block of pyroxene mineral (Mg, Fe)SiO₃ such as enstatite, ferrosilite and hyperthene and the correlation between FeO and CaO may link to other cpx mineral. The correlation between Cr₂O₃ and Al₂O₃ may relate to Cr-in-Cpx (or Cr-diopside) and Al-in-Opx formed in upper mantle or lower crustal region where Cr₂O₃ and Al₂O₃ pyroxene may react with garnet or other minerals at certain thermal-pressure condition [12].

Discussion. The result for MDA analysis has demonstrated that the method works fine for separate different mineral groups for both eucrite and diogenite. Since canonical discriminant diagram can bring all known elements into consideration that has limited the double come from element to element diagram. Samples have been well defined and fall in limited areas in the canonical discriminant diagram are assured to come from (4) Vesta. If this point stands, these MDA result may support a magma ocean hypotheses for the (4) Vesta. However, if sample does not fall in the fields of these groups, it may not form under the same condition. The MDA is powerful statistic method. Although using only major element composition as variables in this study, the MDA in fact can analysis variables from difference source. It can analysis data include major, trace, LREE elements, as well as isotopic ratios in one data base. The correlation between elements and the impact indexes for elements can help us to find the major players in the system and to show the direction of each element may change. This study is the first step of the ongoing study, more new data for unknown HED samples will bring in for MDA analysis in our study. The strong correlation between Cr₂O₃ and Al₂O₃ may be a good subject for further study as well.

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