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RESEARCHES ON SOIL ENVIRONMENTAL BACKGROUND VALUES IN TIBET

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ABSTRACT: The environmental background values of 13 elements of Hg, As, Se, Cr, Mn, V, Pb, Cd, Zn, Cu, Ni, F and Co in xizang soils are obtained through analyzing and determining 205 samples of surface soils in Tibet and the final data processing. The background values of these elements are compared with those of the corresponding elements in the whole China, U.S.A. and Alaska. It is found that the background values of major elements in Tibet soils are higher than the average level of the whole China. The comparison of background values between Alska and U.S.A. shows a similar result. This is because both Tibet and Alaska have a cold climate. Meanwhile, the factor correlation analysis of 13 elements in Tibet soils, organic matter, soil granularity and pH values of Tibet soils are carried out, and *R*–type cluster analysis is made for these 13 elements.

KEY WORDS: Tibet, background values, soil, *R*– type of cluster analysis

Tibet, called "the third pole in the world", is one of the least polluted region and also an ideal site for researches on environmental background values. In 1988, the author of the paper had been there for exploration as a member of scientific exploring team organized by both the Chinese Academy of Sciences and Tibet Environmental Protection Bureau. This is the first time to survey the Tibet soil environmental background values on a large scale and detailedly in our long history. This research has great significance and its fruits will be referred not only in Tibet, but all over the country or the world as well.

Meanwhile, the results from this research are very useful for further researches on the surface geochemistry characterization, the formation and the classification of soil in Tibet.

I. THE OUTLINE OF NATURAL ENVIRONMENT IN TIBET

Located in the south of China, Tibet Autonomous Region is between 26° 52′ to 36° 32′ north latitude and 78° 24′ to 99° 06′ east longitude. Its overall area is $120\times10^4km^2$ or so, accounting for about one eighth of the whole country. The average height above sea level in Tibet is over 4000m. Most of mountains there run from east to west, the well known of which are Himalayas, Gangdis–Lian Tanggula Mountain, Kala Kunlun–Tanggula Mountain and Kunlun Mountain. Hengduan Mountain, located in the east of Tibet Plateau, is the only mountain run from south to north. The overall terrain in Tibet is high in northwest and low in southeast, which can be divided into two levels of highland planes in 4400 to 5000m and 5000 to 5200m above sea level.

The rainfall and climate differences in all Tibet are in great disparity. The rainfall per year in south of Himalayas is up to 3000mm. The average temperature there per year is over 20℃. The rainfall decreases dramatically in the deep internal part of the highlands. In Ali mountainous region, the outmost west part of the highland, the rainfall per year is only 50 to 80mm deep, while the average temperature there per year is 0℃ to 3℃ centigrade degrees. Tibet far and wide region and its complicated geography lead to the diverse climate there. But there also exist some regular patterns there such as warm, hot, wet and moist climate; warm half–moist, cool and half–dry climate; dry–climate; cold and half dry climate, all of which are classified from southeast to northwest.

Corresponding to plateau region differences in water and heat conditions, the vegetation distribution in Tibet has greatly different regular patterns in horizontal direction–such as, in succession, from southeast to northwest are the torrid and subtropical forest zone; grassland zone in mountain and bush; grassy marshland zone in high mountain; grassland zone in high mountain; grassland zone with wilderness and very cold climate; and desert zone with very cold climate. So the vegetations there are classified as one with few and scattered form of high mountain; the one with grassy marshland in high mountain; the one with grasslands in high mountain; the one with grasslands in high mountain; the one with desert in lower mountain; the one with grassy marshland and dense bush; the one with dark coniferous and bright coniferous forest; the one with mixed coniferous and broad leaf forest; the one with long green broadleaf forest; the one with seasonal rainy forest; and the one with grassy marshlands and marsh.

The complicated topographical climate and plant sorts in Tibet lead to its complicated and diverse soil patterns. Tibet has more than ten kinds of soils in distribution, among which, in distribution with larger area are such as yellow earth, yellow–brown, brown soil, dark brown forest soil bog soil sol onchak, subalpine meadow soil, alpine meadow soil

Subalpine steppe soil, alpine steppe soil, alpine desert soil etc., Meanwhile, highland climate and vegetation the with horizontal and, vertical soil difference lead to horizontal vertical distribution zone formation in Tibet, e.g. in succession, from southeast to northwest there are forest soil, grassland soil and desert soil. Attacked by continual cold and dry climate, the formation age of Tibet soil are younger, and its soil parent matter has slighter efflorescence. In the most part of highlands there, the soil contains a large number of gravel and granul substances with greater size, which principally characterize the Tibet soil[1].

II. SAMPLE COLLECTION AND ANALYSIS

1. Sample Collection

Several months have been spent on Tibet soil sample collection for environmental background values after travelling ten thousands of kilometers. All we have collected, are fourteen kinds of soil samples, in which two hundred and five samples are in earth surface and one hundred fifty-six samples are in sublayer.

2. Sample Analysis

The paper will limit the background value analysis within thirteen elements, that is, As, Cr, Mn, V, Pb, Zn, Cd, Cu, Ni, Hg, Se, F, Co, in Tibet soil. To gain reliable and comparable data, the number for the parallel analysis is given more than thirty percent of all samples analyzed. Especially for elements with very lower content or in poor accuracy for analysis, more strict requirements are made on the numbers for the parallel, analysis. The elements As, Cr, Mn, V and Co are measured by neutron activation analysis method in ORTEC HPGE instrument. The element Cd, Pb, Zn, Cu and Ni are measured by flame vapor atomic absorption in PE-5009 device. The element Se is measured by fluorescence spectrophotometer in Rigaku Rs-540 device. The element Hg is measured by cold vapor atomic absorption in F-732 device. The element F is measured by both alkali melting and ion selective electrode method in DF-808 device.

III. RESULTS AND DISCUSSIONS

1. The Environmental Background Values in Tibet Soil

A large amount of calculation had been spent on the original data treatment for the environmetal background values in Tibet soil. IBM-PC/ XT microcomputer had been used and DBACE Ⅲ was used to treat and file the data. Basic Language was used to further treat the data by mathematical statistics.

The level of element content deflection (r) and peak value (p)with the limit of formulae as following: $-3\sqrt{6/n} < r < 3\sqrt{6/n}$ and $-4\sqrt{24/n} < P < 4\sqrt{24/n}$. These above values are used to decide whether one element is either in normal or logarithmic normal distribution. Table 1 shows the sequence arranged for the thirteen elements in sequence from big to small values of content in Tibet soil according to the coefficients of variation. The sequence for the elements are as follows: Hg> Ni> Cr> Mn> As> Cu> Se> Co> F> Cd> V> Pb> Zn. Among these elements, only element V is in normal distribution, the test twelve elements are in or close to logarithmic normal distribution. Also known from Table 1 is that, in nature, absolutely exact distribution is less suitable for one element, which more practical is the approximate distribution for any element. If one element is in logarithmic normal distribution, its geometric mean value is closer to the median value than is the arithmetic mean value (e.g. the median value of element Hg is 0.0215, its geometric mean value 0.021 and arithmetic mean value 0.0255). If one element is in normal distribution, its arithmetic mean value is closer to median value than is the geometric mean value (e.g. the mediam value of element is 76.1, its arithmetic mean value 75.9, its geometric

Table 1 The environmental background values of Tibet soil (mg/ kg, Layer A)*

Element	Distribution	Minimum	Maximum	Mediam	Arithmetic average	Geometric mean	Variation coefficient	Within (95%)
Cu	L	6.4	71.2	19.7	21.9	19.6	49.3	7.74–49.8
Pb	L	9.8	56.1	27.7	28.9	27.6	29.9	14.8–51.4
Zn	L	29.5	149.1	71.9	73.7	70.7	28.5	39.3–127.3
Cd	L	0.011	0.184	0.074	0.08	0.074	35.3	0.033–0.168
Hg	L	0.004	0.188	0.022	0.026	0.021	82.4	0.006–0.0743
Ni	L	2.3	154.6	29.8	32.1	27.8	55.8	8.88–87.2
Cr	L	13.9	316.0	69.6	77.4	68.0	54.7	24.2–191.0
Co	L	1.7	47.5	11.0	11.6	10.4	44.9	3.90–27.9
V	N	21.0	143.0	76.1	75.9	71.9	30.5	29.4–122.3
Mn	L	154	2829.5	586.0	636.0	569	52.3	223–1451
F	L	116	1558	525	542	506	37.3	236–1085
As	L	1.9	51.9	17.2	18.7	16.2	51.8	5.17–50.8
Se	L	0.035	0.365	0.135	0.150	0.133	48.0	0.049–0.365

* Sample number are two hundred and five; L –longorithmic normal distribution; N –normal distribution

mean value 71.9). According to the analysis results above, know is that geometric mean value can give right content level for trace element existing in nature. Most of trace elements in nature are in or close to logarithmic normal distribution, whose content level should be shown by mediam value[2].

2. Comparison of Environmental Background Values in Tibet and Other Regions

The district comparison method is often adopted, especially in analysing geochemistry data. This method makes requirements not only on the comparability in data but also on that in different regions. For example, though Tibet and Alaska of U.S.A. have different geographic latitude, they have many similar aspects such as areas($120\times10^4 km^2$ or so for Tibet, $152\times10^4 km^2$ for Alaska), cold climate and grassland and wild soil. Thus, the two regions have good comparability.

Table 2 The comparison of evenviromental values of soils between Tibet and other districts (mg/ kg)

Element	Tibet		Alaska[3]		China		American continent[4]		Crust abundance value[5]
	GM*	AM*	GM	AM	GM	AM	GM	AM	
Cu	19.6	21.9	24	29	20.0	22.6	17	25	63
Ni	27.8	32.1	24	33	23.4	26.9	13	19	89
Co	10.4	11.6	13	14	11.2	12.7	6.7	9.1	25
Cr	68	77.4	50	64	53.9	61.0	37	54	110
V	71.9	75.9	112	129	76.4	82.4	58	80	140
Mn	569	636	510	670	482	583	330	550	1300
As	16.2	18.7	6.7	9.6	9.2	11.2	5.2	7.2	2.2
Zn	70.7	73.7	70	79	67.7	74.2	48	60	94
Cd	0.074	0.080			0.074	0.097			0.2
Hg	0.021	0.026			0.040	0.065	0.058	0.089	0.089
Pb	27.6	28.9	12	14	23.6	26.0	16	19	12
F	506	542			440	478	210	430	450
Se	0.133	0.150			0.216	0.290	0.26	0.39	0.080

* -Geometric value; AM -arithemetic value.

Table 2 shows that five elements Cu, Co, V, Hg and Se in Tibet are lower in content than that in our whole country. Among them, the content level of element Hg is approximately one half of our country's average. While, the seven elements Ni, Cr, Mn, As, Zn, Pb and F are higher in content level than that in our country's average. Among them, the content level of element As is about two times of our country's average. Comparing Alaska with whole the U.S. continent, the eight elements Cu, Ni, Co, Cr, V, Mn, As, and

Zn in Alaska higher in content level than the average in U.S. continent have been discovered. The two comparisons above have something in common, that is, most of element background values in Tibet or Alaska soil are higher than those in whole China or those in U.S. continent, alternatively. This may be relevant to the fact that, under the condition of very cold climate, the soil in both Tibet and Alaska are in nature rough backbone clay with gravel because of weak physical and biological efflorescence. And also, the elements there are less-migrated and less-washed during soil formation by efflorescence. Besides, among the nine elements compared in Tibet and Alaska, the background values from elements Cu, Co, and V in Tibet are lower than these in corresponding soil in Alaska.

The background values from the four elements Ni, Cr, Mn and Zn in Tibet soil are closer to earth's crust abundance values than these in Alaska soil.

3. Factor Correlation Analysis

Soil is formed during long period of mineral, physical, biological and chemical efflorescence, and evolution in the crust surface. In this long period, elements took part in the process of oxidation and reduction, exchange absorption, washing and complex deposit, and decomposing under the action of factors such as climate, biology and topography. The elements are reorganized during the formation of soil to form chemical composites with other elements different from these in parent substances of soil. Meanwhile, the chemical composites from soil elements have essential relationship to the parent substances and physical chemical properties of soil. There also exist intrinsic relationships among different elements. To discover the intrinsic regular patterns existing in chemical composites by soil elements, the paper makes correlation analysis on the thirteen elements, organic substances and grain size in Tibet soil.

Table 3 shows that soil grain size is an important factor affecting element background values in Tibet soil. Among thirteen elements measured, most are in negative correlation with grain size from 0.1 to 0.001mm in diameter. And also, among these above, the elements Hg and Mn are in notably negative correlation with grain size. Elements Ni and Co are in extremely negative correlation with grain size. Opposite to these results from thirteen elements measured before, twelve of them are in positive correlation with grain size from 0.01 to 0.001mm in diameter. The elements Se and Mn in them are in notably positive correlation with grain size. Elements Ni, Co and Hg are in extremely positive correlation with grain size. But, the correlation coefficients of most elements have less notable correlation with grain size fewer than 0.001mm in diameter. Only the element Co in them is in great positive correlation with grain size. These results above demonstrate that the content level of all thirteen elements in Tibet soil has very close relations with the grain size of soils there.

Generally, most of soils rich in gravel are low in content level of trace elements, while soils with grain size from 0.01 to 0.001mm are higher in trace element content. It should be pointed out that the correlations of element content level with grain size fewer than 0.001mm are not as good as these with grain size from 0.01 to 0.001mm. The reason for this may be that the Tibet soils have lower content level of grain size fewer than 0.001mm, and method for analysing itself exists errors.

Table 3 Correlation matrix of environmental background values of Tibet soil in layer A

	Cu	Pb	Zn	Cd	Ni	Cr	Hg	As	Se	Co	V	Mn	F	OM	pH	P_1	P_2	P_3
Cu	1																	
Pb		1																
Zn	++	++	1															
Cd		++	++	1														
Ni					1													
Cr	+				++	1												
Hg							1											
As		+	++	++				1										
Se		++	++				++		1									
Co	++	++	++		++	++			+	1								
V	++	++	++			+	+		++	++	1							
Mn	++		++			+				++	++	1						
F	+	++	++						+	++	++	++	1					
OM		+					++	–	++			+	+	1				
pH							--	++	—		–		—	--	1			
P_1					—		–			—		–				1		
P_2					++		++		+	++		+		+	—	—	1	
P_3										+						—	++	1

Note: Variation examination: "+, –" (a = 0.05); "++, —" (α = 0.01); n = 102, OM –organic; p1 –0.1 to 0.01mm in grain size; p2 –0.01 to 0.001 mm in grain size; p3 –less than 0.001mm in grain size.

The correlation analysis in Table3 shows that the organic substance and elements Mn, F and Pb are in great positive correlation with elements grain size, in extremely positive correlation with elements Hg and Se, and in notably negative correlation with element, as in Tibet soils. Besides, the organic substances in soils are in positive correlation with grain size from 0.01 to 0.001mm, and in great negative correlation with pH value of soils. These results above demonstrate that, under environmental interaction, the migration, transformation and dispersion of elements in soils are affected by organic substances and acidity in soil in this or other way because of physical and chemical properties of elements themselves. It is these reasons above that make the chemical composites of Tibet soil elements different from these on parent soil element.

3.4 *R*-Type of Cluster Analysis

The relations among organic substances, pH values, and grain size in thirteen elements of Tibet soil have been studied above. The paper now proceeds the *R*-type of cluster analysis for these thirteen elements based on the factor correlation analysis results above in order to further discover the intrinsic regular patterns in elements. In *R*-type of cluster analysis, the paper adopts the classification method of step-by-step cluster. This method is better than both one step cluster and δ-type of step-by-step cluster method in accuracy. The former one avoids the unreasonable cluster results from the latter two, especially, when there are more than ten factors. Due to large amount of computation in step-by-step cluster analysis, microcomputer has been adopted to combine every cluster one by one. The final good correlation numbers ($n-2=100$; $r_{0.01}=0.254$) will intercept dendrogram (see Fig.1).

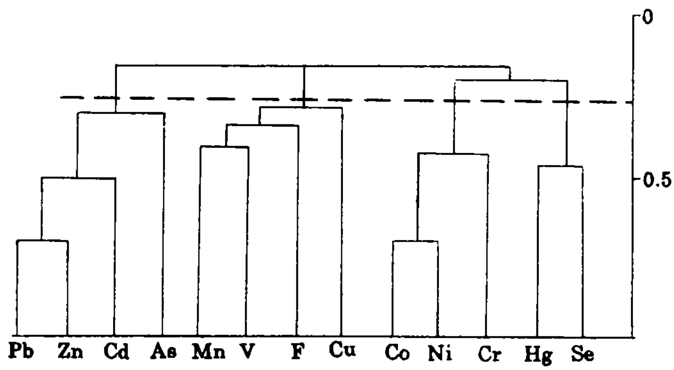

Fig.1 Thirteen elements cluster of *R*-type in Tibet soils (layer A)

Fig.1 shows that the good correlations of thirteen elements in Tibet soil can be intercepted horizontally. And four groups of elements will be given as fellows: (1) the elements Pb, Zn, Cd and As; (2) the elements Mn, F, V and Cu; (3) the elements Co, Ni and Cr; (4) the elements Hg and Se.

The first group is characterized by these following common points such as, closely similar geochemical performances for elements in internal growth, and close relations between elements in formation of rocks. The elements Pb, Zn, and As except Cd are copperophilic. The elements Pb closely coexists with Zn in internal growth. The element Cd often displaces Zn in soil because of their analogous nature. While sulphur-containing negative ions such as element As is easy to combine with metal element Zn to form mineral salt containing sulphur. The second group is characterized by following-these elements great in solubility and dispersion, and easy in migration and accumulation in surface growing environment. Element F is a mineral agent which is easy to combine with metal element to form a soluble compound migrating in the surface. In the surface, the growing minerals from V-containing element are attacked by efflorescence and element V is oxidized to transformed into V^{3+}, which is transformed into V^{5+} ion to form another ion $(VO_4)^{3-}$. The salt from ion $(VO_4)^{3-}$ is soluble and can migrate in solution with great variations of acidity or alkality, especially in surface soil. While element Mn will be easy to reduce and its absorption by soil will be weakened so that it migrates with water.

Some closely coexisting elements often perform different geochemical properties in internal growth. This greatly results from their differences in physical chemical properties such as ion radius, solubility in water, the way of migration, and different migration speed. The element Cu will be separated from copperophilic elements in minerals during formation of soil, while it will cluster with elements Mn, Vand F in surface environment. The reason for this is that element Cu is easy to combine with ion SO_4^{2-} to form compound $CuSO_4$ which is easy to solve in water and migrates far away by surface water. In surface growing belt, the more the element Cu oxidizes or the greater acidity of its solution is, the greater the element Cu migrates or the stronger the ability for it to accumulate is. Besides, the element Cu has good correlation with element in ferrofamily such as Cr, Co and V. The reason for this may be that these elements above and element Cu are in the same position of the periodic Table, and they have similar ion radii. So, these elements have similar geochemical properties and performances in surface environment.

The third group has such special points as that the elements Co, Ni, and Cr belong to the same ferrofamily. They have closely similar geochemical performances in internal and surface growing. The element Ni and Co have ferrophilic and suphurophilic properties. There exists a very common exchange and displacement phenomenon in them. They have similar regular pattern in abundance value distribution in crust. In the surface soil, the elements Co, Ni and Cr have negative correlations with organic substances and are easy to solve and to migrate in humic acid.

In the fourth group, the element Hg in nature exists greatly in compound $(HgSe)_{20}$ [6], though element Se and Hg are not in the same group of element geochemistry. In surface belt, they are easy to be absorbed by media. Table 3 shows that these two elements have notably positive correlations with grain size from 0.01 to 0.001mm in soil, and extremely notably positive correlation with organic substances in soil. These demonstrate that elements Hg and Se not only form their minerals each other in internal growth, but also have closely similar geochemical performances in surface growing, that is, they both have a tendency to accumulate in both organic substances in soil with fine grain size. Moreover, this tendency will be more and more notable with the increasing of soil acidity.

The conclusions from all above analysis are such that, the classifications of elements from four groups above are not irrelevant combinations. These classifications have revealed, to some extent, the incluse -exclusive relationships in element geochemical properties and their chemical complex characterizations during their internal growing of minerals. Moreover, some regular patterns in different elements in migration or clustering are also discovered, e.g. in surface soils.

In a word, the cluster dendrogram in this paper has essentially revealed the relations of both coexistence and combinations from thirteen elements in Tibet soil. And elements in each group above are showing common points and differences in surface enviroment and during formation of soil by dendrogram.

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