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The Complex Networks of Earth Minerals and Chemical Elements.

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Abstract

We study the large-scale organization of the mineral-mineral (MMN) and element-element (EEN) complex networks by analyzing their topological structures. We see that the MMN and EEN are homogeneous, display large cliquishness, small average path length and large average degrees. Most of these networks display uniform degree distribution with the exception of the weighted EEN, which display a power-law degree distribution with exponential tail. All these topological characteristics appear to be consequence of the evolutionary mechanisms giving place to the minerals on Earth mantle, which as a whole display a relatively uniform major element composition. We also study the correlations between some topological network parameters and the abundance of chemical elements in different scenarios. Good correlation is obtained between the weighted degree and the abundance of elements in Earth's crustal rocks.

1 Introduction

The study of complex systems has become one of the most important areas of multidisciplinary research in the XXI century, pervading scientific disciplines from biology and ecology to technological and social sciences [1-5]. A common characteristic of these complex systems is that they can be represented by means of complex networks [1-5]. This characteristic simplifies the analysis of these systems by representing the systems' objects by nodes and their interactions by means of links connecting pairs of nodes. However, there are other characteristics of complex systems that make their modeling a more difficult task. In particular, it is known that complex systems are formed by different elements which also constitute complex systems. For instance, when analyzing complex ecological systems we usually concentrate only in a tiny part of them, which indeed are complex systems. One of such

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systems are the food webs in which different species are represented by the nodes and their trophic relations are the links of the networks [6]. However, as plants form part of these systems it is necessary to understand the characteristics of the soils in order to analyze how the plants obtain nutrients [7,8]. In fact, soil characteristics depends very much on the mineral composition existing in them. Thus, at the bottom of this scale we will find the network of the chemical elements existing on Earth, which form the minerals and supply the nutrients to the plants and then to animals through the food chain [9]. In conclusion, at the bottom level we are dealing with complex networks of interest for chemists. Despite this evident basic relationship between Chemistry and the study of complex networks only very few studies in this field involve the study of chemical objects. The main exception is the study of complex reaction networks with a large tradition in chemical graph theory [10,11]. Consequently, we will start here a series of applications of complex networks in Chemistry starting by the study of the Earth's minerals and chemical elements networks.

Minerals are the natural sources for the chemical elements on Earth. The chemical elements are particularly important for the development of all chemistry on our planet and their availability is essential for the evolution of living systems [12]. Thus, the study of the complex system of minerals and chemical elements on Earth is primordial to understand the origin and development of life as well as for a better comprehension of the ecological cycles in our planet [11-14]. In addition, the understanding of the complex relationships between minerals and elements can give some insights about the formation and evolution of the Earth [17-23].

Consequently, we propose to use the general approach of complex networks to explore the large-scale topology of the mineral-mineral and element-element complex networks associated to the chemical composition of the Earth [21-23]. The study of these networks is not only important for understanding the organizational principles of larger scales networks, like the mentioned ecological systems, but also to motivate the study of the organization and evolution of minerals/elements on our planet from a network perspective. The current work is organized in three main parts. The first part is dedicated to the explanation of the principles for the building of the minerals/elements complex networks. Then, there are two sections dedicated to the topological analysis of the mineral-mineral and element-element networks, respectively. In every case we bring some links between network topology and the organization/evolution of minerals and elements on Earth.

2 Data sources and methodology

A mineral-chemical element network (MCEN) can be viewed as a bipartite graph [24] where minerals and chemical elements are the nodes forming two disjoint sets. One set of nodes is formed by those representing minerals and the other is formed by the nodes representing chemical elements. A link connecting a mineral and a chemical element represents the existence of this element in the composition of the mineral. Lets take for instance hercynite, which has the following empirical formula: $\text{Fe}^{2+}\text{Al}_2\text{O}_4$. This mineral is represented in the network by a node which is connected to the nodes representing Fe, Al and O. In the Figure 1A we illustrate an example of MCEN for four minerals and six chemical elements. The real MCEN is formed by 4443 minerals and 78 chemical elements existing on Earth. The total number of chemical elements identified on Earth is 83 [25], but here we exclude from the study five Noble gases (^4He , ^{20}Ne , ^{36}Ar , ^{84}Kr and ^{132}Xe), which makes the 78 elements included in our work. The dataset was compiled from the database of minerals by chemical composition (<http://webmineral.com/>). The search was carried out by chemical elements. If searched by alphabetical listing using the item “All” of the database there appears only 4442 minerals because Na-komarovite is not reported. We have confirmed this difference by conducting an updated search on August 21, 2007.

The MCEN can be projected on two different spaces. In one of the projections we obtain a mineral-mineral network (MMN) in which the nodes represent minerals and two nodes are connected if the corresponding minerals share a chemical element. The other projection renders an element-element network (EEN) where nodes represent chemical elements linked together if they appear in the same mineral. In reality these two networks are multigraphs, i.e., graph having multiple links between nodes. For instance, in Figure 1B we illustrate the MMN formed from the MCEN given in Figure 1A. It can be seen that majorite and hercynite share three links, which is a consequence of the fact that these two minerals contain three chemical elements in common. The same happens for the EEN illustrated in Figure 1C where there are chemical elements connected by two links because they appear simultaneously in two minerals. Hereafter we will refer to the networks having multiple links as weighted networks. The weights are the integer numbers representing the multiplicity of the links which connect pairs of nodes. When we do not consider multiple links for the analysis we will refer to the corresponding graphs as binary or simple networks.

The simplest network property that we can analyze is the node degree [24]. The degree of a node is the number of links incident to it. We use the symbols $k(i)$ and $k_w(i)$ for the degree of the node i in the simple and weighted networks, respectively. The degree of a node is the

number of links incident to it. In a weighted network it corresponds to the sum of weights for all ties connected to this node. For instance, if we pick up a mineral in the MMN of Figure 1B we will find that it shares at least a chemical element with three other minerals because its average degree is $\langle k \rangle = 3$. Another useful measure of network topology is the *average path length* $\langle L \rangle$ [26], which is defined as the average minimum distance d_{ij} between any pair (i, j) of nodes:

$$\langle L \rangle = \frac{1}{N(N-1)} \sum_{\forall i,j} d_{ij} \quad (1)$$

This measure is applicable only to connected networks as the distance between disconnected nodes is not defined. Fortunately, the networks considered in this work are connected. That is they corresponds to networks in which a path can be defined between any pair of nodes. The average path length gives an idea of how many steps are necessary on average to travel from one node to another in the network. The density of links in the neighborhood of a node i or cliquishness is characterized by means of the so-called clustering coefficient, C_i [26]. It characterizes the fraction of neighbors that are also neighbors of each other or the transitivity of the relationships between nodes. We will use here the clustering coefficient defined by Watts and Strogatz [26]:

$$C_i = \frac{\text{number of triangles connected to node } i}{\text{number of triples centered on node } i} \quad (2)$$

The symbol $\langle C \rangle$ will be used for the average of C_i .

3 Topological properties of the MMN

The simple MMN has 4443 nodes and 5635264 links, which gives an average degree $\langle k \rangle = 2536.69$. This means that on average every single mineral share at least one chemical element with other 2537 minerals. That is, on average, more than half of the minerals on Earth shares at least one chemical element among them, which is of course a consequence of the larger number of minerals in comparison with the number of chemical elements existing. When the weighted MMN is considered the average degree is $\langle k_w \rangle = 4504.80$, which indicates that on average every mineral shares one or more chemical elements 4505 times with other minerals in the network.

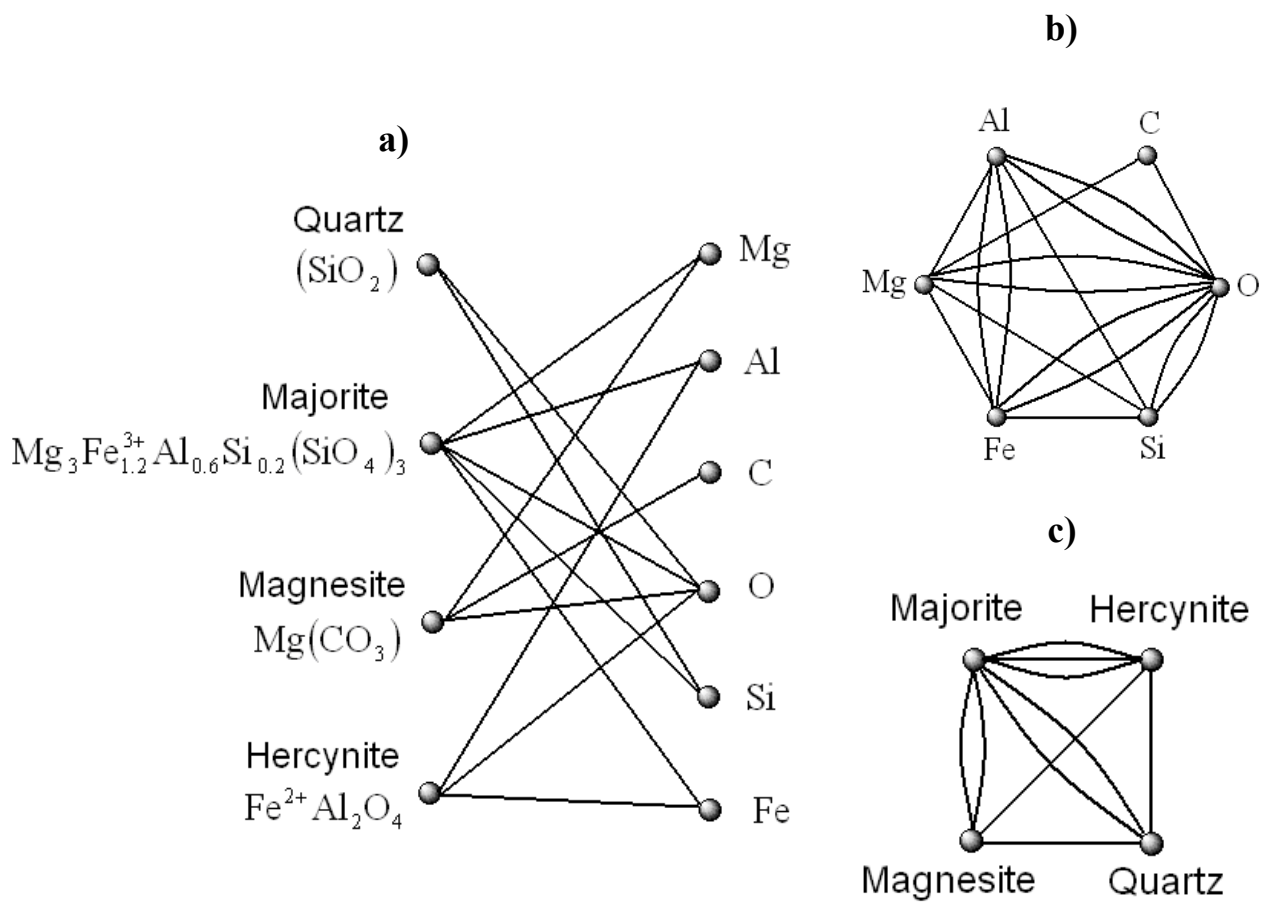


Figure 1. a) Illustration of a bipartite network of minerals and chemical elements in which nodes are minerals/elements which are linked if a mineral contains the corresponding element. (b) The mineral-mineral network derived from the bipartite network illustrated in (a). (c) The element-element network derived from the bipartite network illustrated in (a).

However, this mineral will share one or more chemical elements on average 5 times with other minerals because $\langle k_w \rangle = 5$. The values of both average degrees k and k_w are related to each other as can be seen in Figure 2.

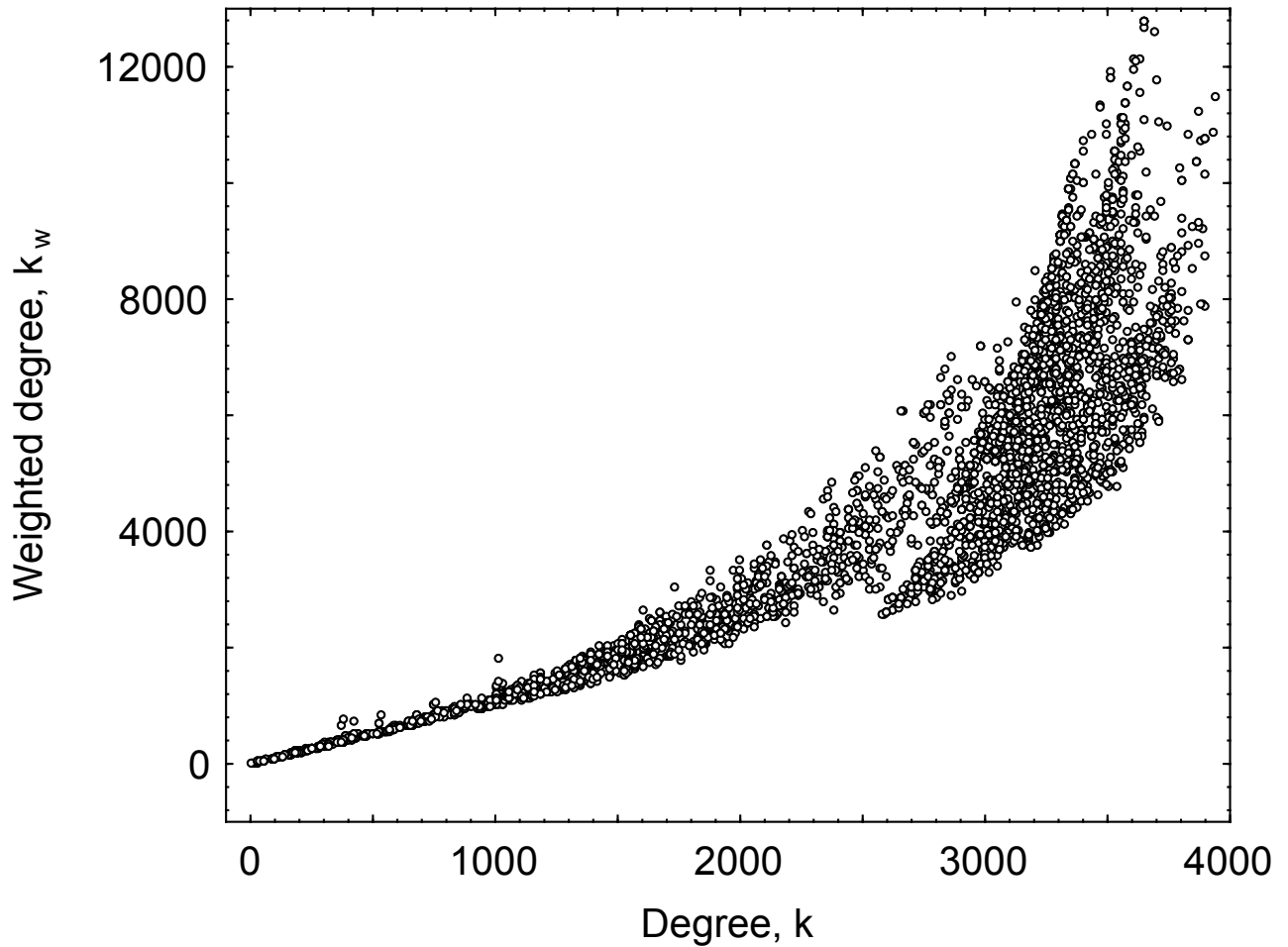


Figure 2. Correlation between the degrees of the weighted and simple mineral-mineral networks.

The values of both $\langle k \rangle$ and $\langle k_w \rangle$ suggest that the generality of minerals on Earth display significant compositional homogeneity. In addition the MMN displays a very small average path length $\langle L \rangle = 1.536$ and a very large clustering coefficient $\langle C \rangle = 0.823$ indicating a very large cliquishness among the nodes. This homogeneity could be a consequence of the disproportion existing on the number of minerals (4443) and chemical elements (78). However, heterogeneous mineral-mineral networks can also be formed by using such disproportion between the number of elements and minerals. For instance, imagine a network in which there are two large clusters of minerals, one formed by a set X of elements and other formed by a set Y of different elements. Then, if the number of elements shared between the two clusters of minerals is very low the network is modular, i.e., not homogeneous. This hypothetical situation is represented graphically in Figure 3.

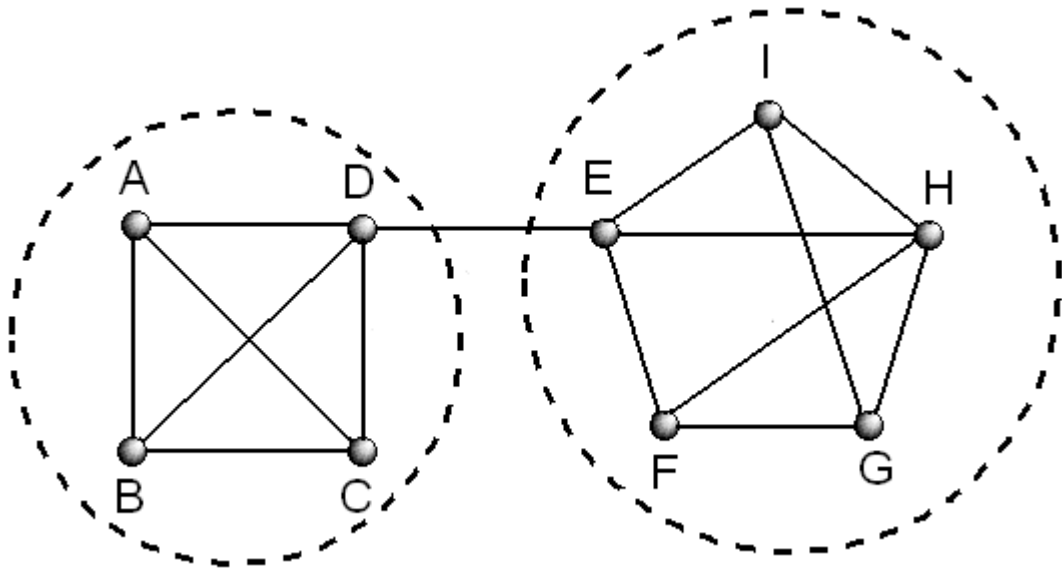


Figure 3. Illustration of a heterogeneous network in which some minerals form highly connected clusters displaying low connectivity between clusters.

The lack of a modular structure similar to the one illustrated in Figure 3 for the MMN has been checked here by using the spectral scaling method (SSM) [27-29]. According to SSM a network is homogeneous if, and only if, there is a perfect scaling between a local and a global topological characteristic of the network (for details see [27,28]). We have observed such a perfect scaling for the MMN studied here (data not shown), which demonstrate its large homogeneity. The topological homogeneity of MMN is in full agreement with the geological record of modern plate tectonics for the last 3.8 Ga which argues for considerable whole mantle stirring for the last few billion years [30]. This stirring is assumed to be the main cause of the relatively uniform composition of the mantle [21,30,31], which produces the observed topological characteristics for the MMN. Another characteristic feature of the MMN that confirms the relatively uniform distribution of chemical elements on the Earth minerals is the cumulative degree distribution. Despite many complex networks display power-law degree distributions the MMN display a rather uniform distribution of the number of links per node as can be seen in Figure 4.

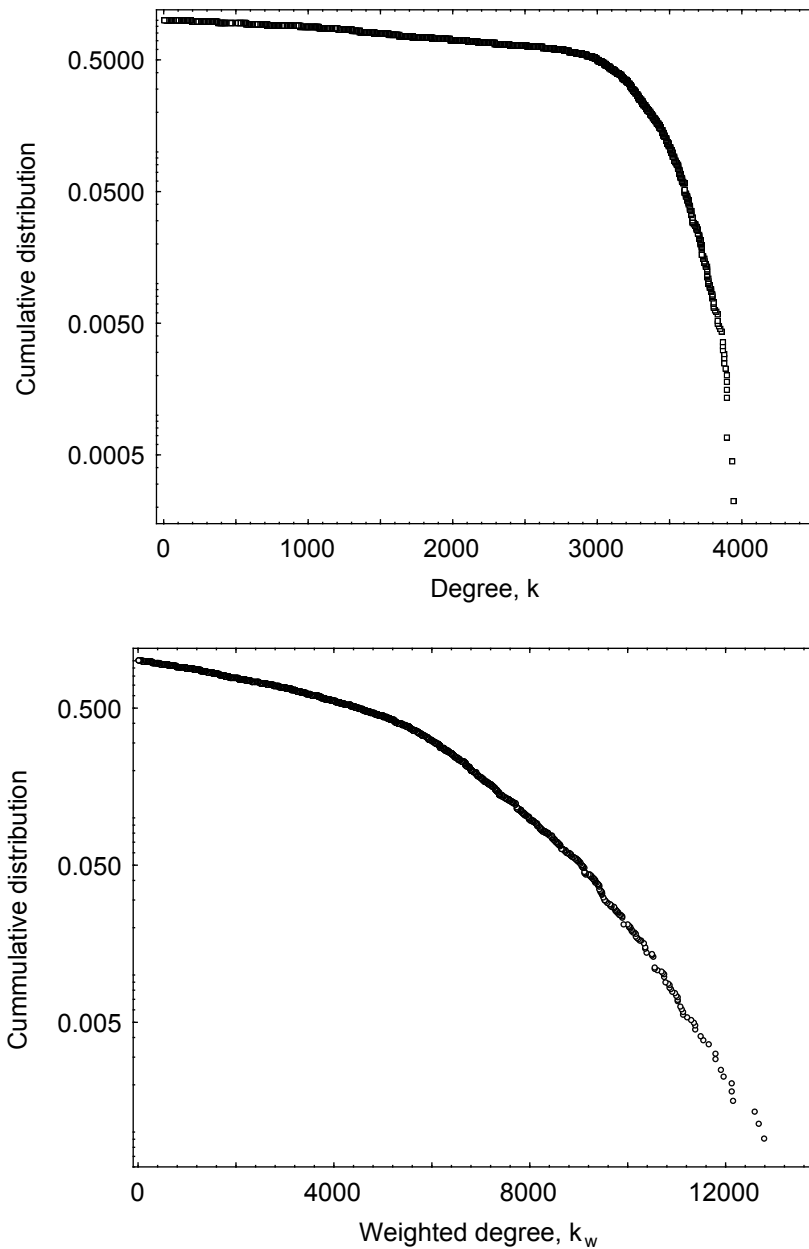


Figure 4. Plot of the cumulative degree distributions for the simple (top) and weighted (bottom) mineral-mineral network.

On the other hand, the large average degree for minerals in the MMN is not a direct consequence of the number of chemical elements forming each mineral. In Figure 5 we plot the degrees, k and k_w , as a function of the number of chemical elements in the mineral. It can be seen that there is a trend indicating that as the number of elements in the mineral increases the number of links the mineral has in the network also increases, particularly when k_w is considered. However, the most connected minerals — haineaultite, kemmlitzite, delvauxite, and others — are not the ones containing the largest number of chemical elements. These

minerals share chemical elements with other 14, 12 and 9 minerals in the network, respectively. However, there are minerals, such as ciprianiite, georgbarsanorite, and khristovite which share elements with 27, 24 and 24 other minerals, respectively, and are not the most connected in the network.

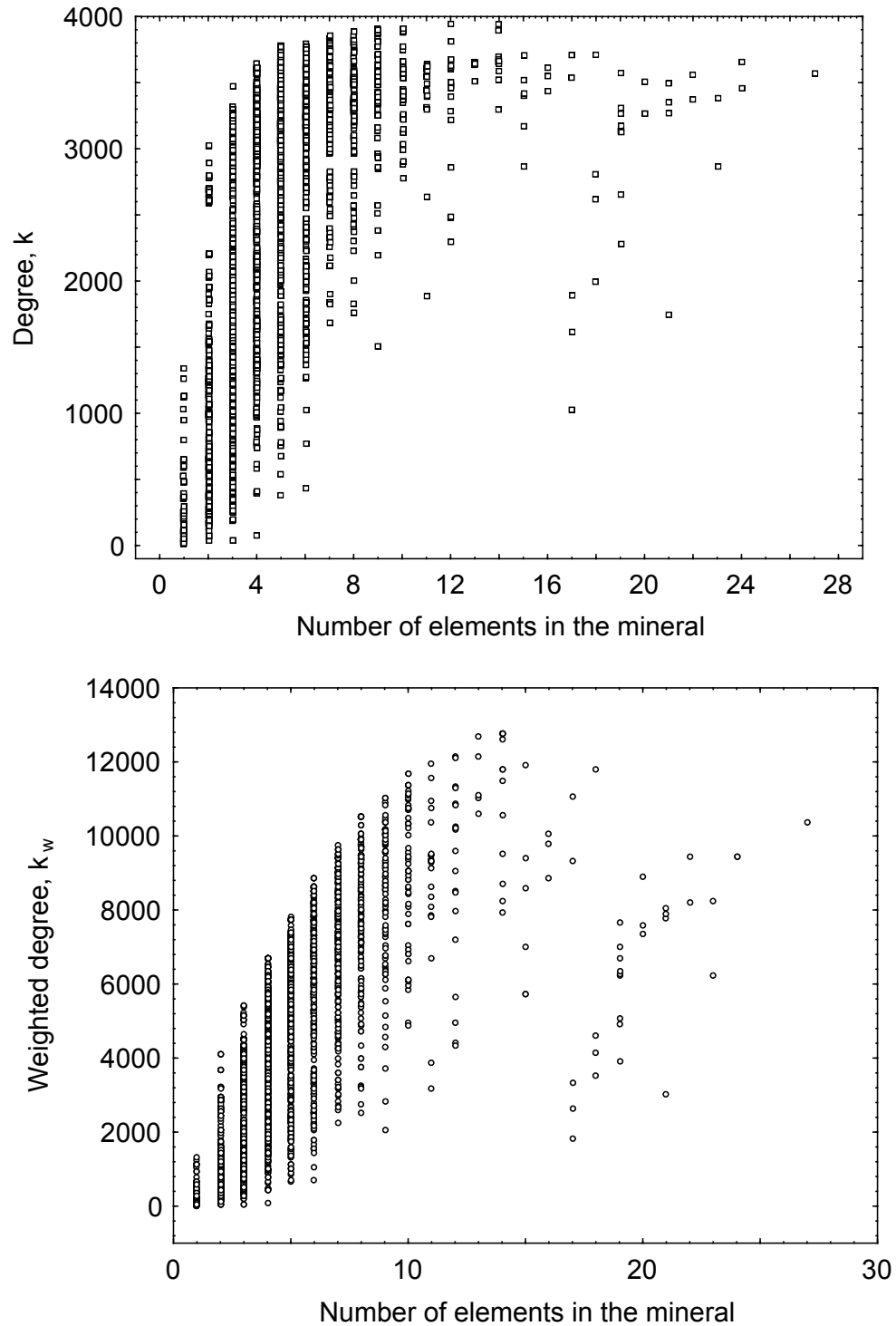


Figure 5. Scatterplot of the number of chemical elements per mineral and the degrees of the simple (top) and weighted (bottom) mineral-mineral network.

This situation can be understood by considering the differences in affinity of the chemical elements forming these minerals. There are elements which form part of a very large number of minerals while others appear in a very limited number of them. As an example take the minerals containing only one element. As can be seen in Figure 5 these minerals display a large range of degree values. For instance, Rhenium and Silicon appear as native elements on Earth, which make them minerals with only one chemical element. However, while Rhenium is connected only to other two minerals in the MMN, Silicon appears in 1322 other Earth minerals. Consequently, the information contained in the number of links per node in the MMN is not duplicated by the number of elements in the mineral.

4 Topological properties of EEN

The complex network of chemical elements is formed by the 78 elements existing on Earth [25] which share 1649 links among them (see Figure 6A). This network has average degrees $\langle k \rangle = 42.28$ and $\langle k_w \rangle = 1366.95$. Similarly to the MMN it displays very low average path length and a large clustering, $\langle L \rangle = 1.454$ and $\langle C \rangle = 0.832$, all indicating a large homogeneity of the network, which was also proved by using the SSM [27-29]. In EEN every chemical element appears in combinations with other 42 elements in the minerals existing on Earth, forming pairs, triples, quadruples, etc. On average every element appears about 1367 times together with other elements in the Earth minerals. Both types of degrees are related to each other by an exponential relation, which can be seen in Figure 6B. However, both measures give different information about chemical elements. Iron and sulfur are identified as the most connected elements according to k . It means that these elements appear in the largest number of combinations with other elements in Earth minerals. Iron is an abundant element on Earth crust [32] and it forms combinations with many other elements forming the so-called “iron minerals”, while sulfur forms sulfides and sulfates with almost all metallic elements. Consequently, the large affinity of Fe and S for other chemical elements produces very large number of combinations of these elements with others in minerals, giving rise to the large value of k observed.

A different picture is offered by the weighted degree, k_w , which identifies hydrogen and oxygen as the most connected elements in the weighted EEN, followed by silicon, calcium and aluminum. The large weighted degree of hydrogen and oxygen in the EEN can be understood by considering the presence of hydroxyl and water in a large number of minerals [33,34]. It is known that most minerals of Earth's upper mantle contain small amounts of hydrogen, structurally bound as hydroxyl. It is contained in different concentrations depending on the minerals and appears in pyroxenes, garnets, olivines and nominally anhydrous minerals, which constitute a significant reservoir for mantle hydrogen, possibly accommodating all water in the depleted mantle [35-37]. Consequently, these two elements appear together in a very large number of minerals. In addition, oxygen forms a large variety of oxides, which also increases the value k_w for this element. These differences between both types of degrees are well accounted by their cumulative distributions. In Figure 7 we show the log-log plot of the cumulative degree distributions for both degrees, where it can be seen that k displays a uniform distribution while k_w has a power-law with exponential tail [38].

The uniform distribution of k indicates that within EEN almost all chemical elements are connected to approximately the same number of other elements in the Earth minerals. There are exceptions like Re, Os and Ru, which are connected to very few other elements, but most of the elements are connected to between 20 and 60 other elements (the average connectivity is 42). The situation is quite different for the weighted degree, k_w . This network property follows a scale-free distribution [39], which indicates that there are many elements with a low number of connections in the weighted EEN and only a few with a very large value of k_w . The number of weighted connections decreases as a power-law up to a value of $k_w \approx 6000$ and then it decreases rapidly following an exponential law with a correlation coefficient larger than 0.99.

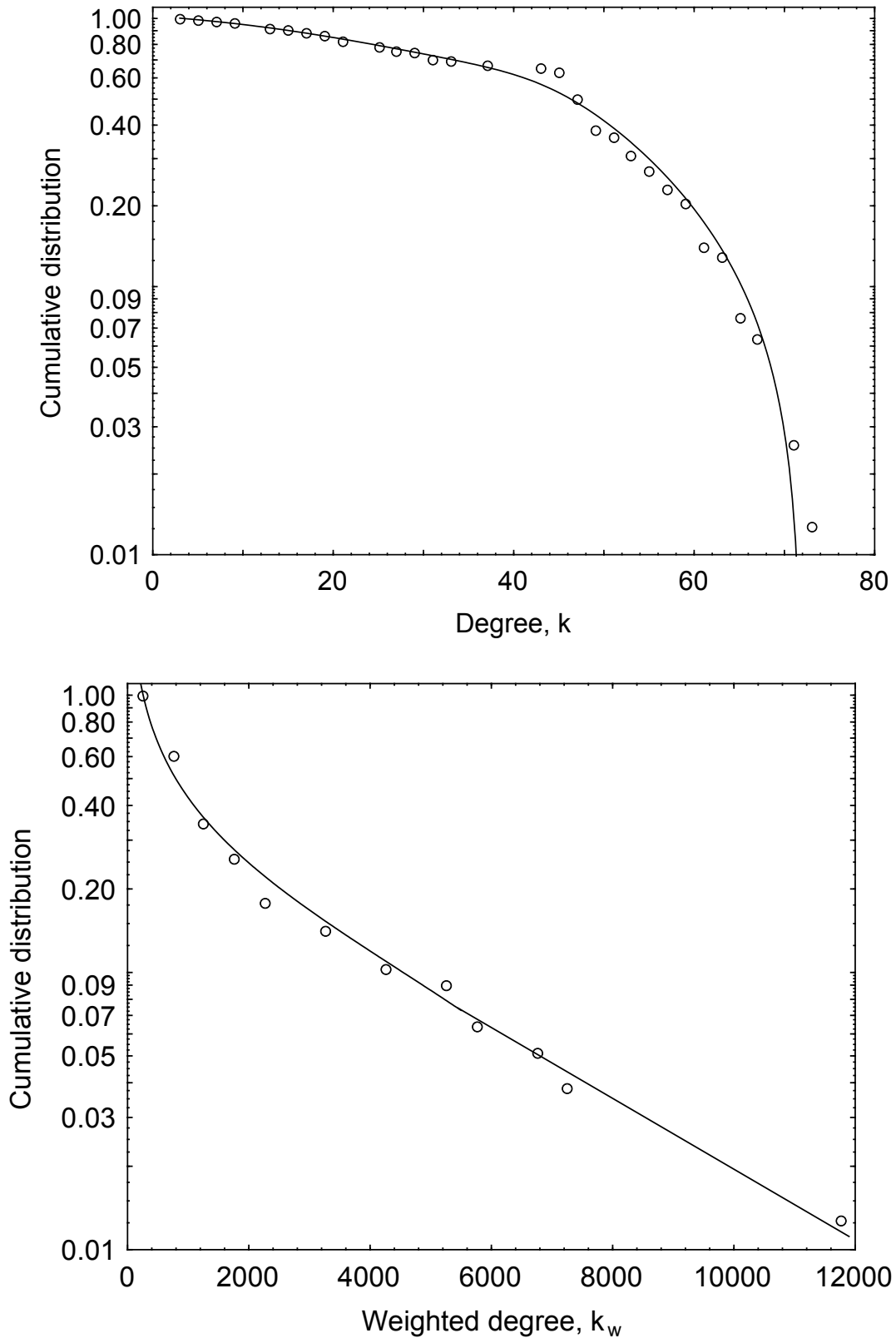


Figure 7. Plot of the cumulative degree distributions for the simple (top) and weighted (bottom) element-element network. The top plot is characteristic of a uniform distribution and the bottom one is typical of scale-free distributions with exponential tail.

The chemical elements which fit to the exponential law correspond to H, O, Si and Ca. In addition to the previously observed characteristics of H and O these results agree with the known fact that the continental crust is principally made up of quartz, feldspars and some mafic minerals, which are rich in Si, Ca, and Al, among others. In particular Ca and Si appear combined in many types of silicates, which are abundant on Earth crust [21-23].

An important characteristic of the scale-free degree distributions is that they are consistent with preferential attachment mechanisms for network evolution [40]. In such models of network evolution the nodes are added to the network by connecting them to the nodes already having the largest connectivity. In other words, in preferential attachment there is a “rich get richer” effect. If we consider a hypothetical growing mechanism for the EEN in which, for instance, Si and O are combined to form silicates (SiO_4) and H and O are combined to form hydroxyl and water (OH and H_2O), then new elements start to be connected to these three elements at a fast rate. For instance, any element forming a silicate will be attached to Si and O, making that the weighted degrees of these two elements grow very fast. The same happens for minerals containing OH and H_2O , which will increase the degree of H and O. As a final consequence these four elements are getting richer each time, making them the real “hubs” of the network, which will display a power-law degree distribution.

Finally, we analyze the correlations existing between the weighted degree and the abundance of chemical elements in Universe, the Sun, and carbonaceous meteorites, as well as in the sea, streams and crustal rocks of the Earth. In all cases we use the abundance of the elements in parts per billion (ppb) by atom. The data were selected from the compilations reported in the web of chemical elements (<http://www.webelements.com/>), where appropriate references to the original sources can be found.

In Figure 8 we illustrate the correlations found plotted in log-log scale. As can be seen in this figure the abundance of chemical elements in the Universe, the Sun and in carbonaceous meteorites only correlates modestly with the number of times that a chemical element appears together with other(s) in an Earth mineral, k_w . The correlation of the weighted degree and the abundance of elements in the sea is very poor indicating that the mechanisms keeping the element concentration in seawater are different from those of continental crust. It is well-known that seawater is considerably more enriched in Na, Cl, and K than the continental crust. In fact, the chemical composition of oceans depends on a large mixture of inputs and outputs fluxes of chemical elements, which include riverine and groundwater flows, Aeolian deposition, rain, hydrothermal circulation, extraterrestrial infall, sediment diagenesis,

evaporation, formation of sea spray, and sea burial. As a consequence there are elements like Na, Sr, Rb, and K which are very soluble and resist to be lost from seawater from some of the before mentioned mechanisms. Others are, however, more easily removed, like Co and Ir which are extremely reactive with particles and decrease their concentration in the seawater. When analyzing the chemical abundance of elements in freshwater there is apparently a better correlation with the weighted degree ($r = 0.63$). However, this correlation is in a large extension due to the large abundance of H and O. If these two elements are removed from the correlation the coefficient drops up to $r = 0.57$. However, this correlation is still different from that obtained for the abundance in seawater when H and O are removed ($r = 0.48$). These differences are a consequence of the dissimilarity in abundance existing for some elements in both reservoirs. The most critical values are those for Na and Cl, which are about 10^4 times larger in seawater than in freshwater. Despite most of the dissolved chemical constituents or salts found in seawater have a continental origin, seawater is not fresh like river water because of the huge accumulation of salts by evaporation and the contribution of raw salts from the land. Other factors increasing salt concentration in seawater are those dissolved from rocks and sediments below its floor as well as because of the role played by marine life in ocean water's composition [41]. All these factors make that the abundance of chemical elements in fresh water correlates better with k_w than the concentration of these elements in the sea, where more variation in the composition has taken place over the years. The best correlation, however, is obtained between k_w and the abundance of elements in crustal rocks ($r = 0.77$). Of course, the largest the abundance of an element in the crust the largest its chance of being combined with other different elements to form minerals. However, as can be seen in this figure there are significant differences between both measures for the range of $50 \leq k_w \leq 1000$ indicating the existence of different mechanisms controlling the combination of elements in minerals.

5 Conclusion

Using the general approach of complex networks we have studied some of the topological properties of minerals and chemical elements networks. Both networks, the mineral-mineral and the element-element networks, share similar topological characteristics. In particular, they are highly dense networks displaying large average degrees, very large clustering and small average path length. These topological characteristics are the consequence of the evolutionary mechanisms giving place to the minerals on Earth mantle, which as a whole display a relatively uniform major element composition.

We have also found a good correlation between the number of times that a chemical element appears together with other(s) in a mineral and the abundance of such element in the crustal rocks. However, the lack of a perfect correlation indicates the existence of other mechanisms allowing the incorporation of a chemical element into a mineral. On the other hand, the lack of correlation between this network property and the abundance of chemical elements in seawater is indicative of the different input-output mechanisms changing the elemental composition in the Sea. In closing, we hope that the current work stimulate the use of complex networks strategy for studying Earth minerals science.

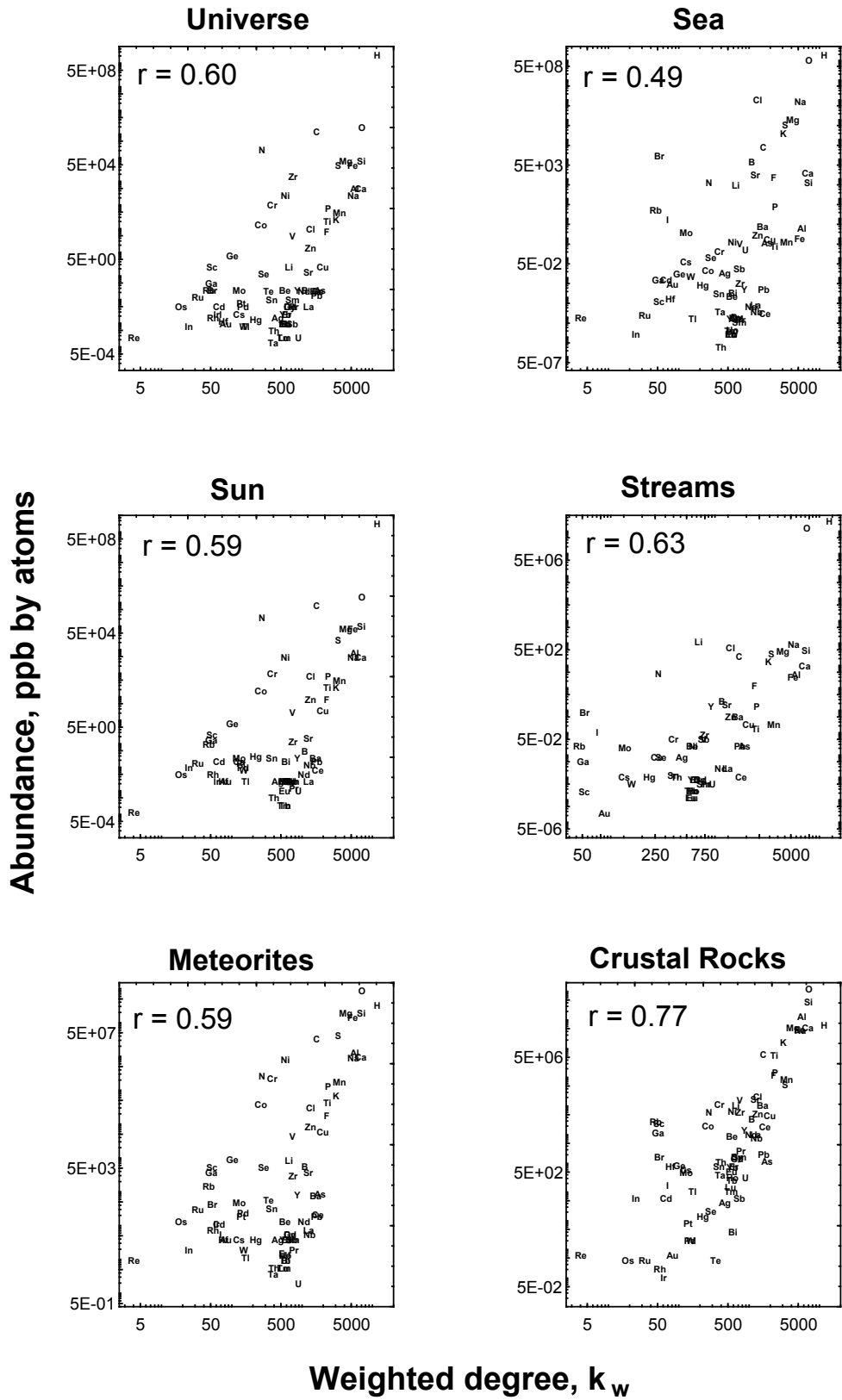


Figure 8. Correlations between the weighted degree of the element-element network and the abundance of chemical elements in the Universe, Sun, and carbonaceous meteorites, as well as in Earth’s seawater, streams and crustal rocks.

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