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A BRIEF NOTE ON MINERAL EVOLUTION AND BIOCHEMISTRY

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ABSTRACT

The natural inorganic materials (minerals and rocks) exceed the limits of the Earth. Therefore, the geology, which is the study of the Earth, represents only a small part of the natural inorganic world. Certain questions about the genesis of the universe are related to the evolution of our solar system and the evolution of life on our planet. In this paper, recent contributions from experimental physical natural-sciences to the formation of the universe (about 15 billion BP) coupled with the occurrence of minerals (4 million years BP) and the biochemical appearance of life (not more than 3 million years) on the Earth are discussed. When Earth was formed, none of the more than 4,400 minerals we know today were existed. Cosmologists estimate that nearly ten billion years after the Big Bang the first elements produced by the melting process. The geological history of mineral evolution on the Earth is an interesting tool to study terrestrial and/or extraterrestrial mineralogy in regard to astronomy, biology, chemistry and other experimental natural sciences.

1. Introduction

The aim of this article is to relate the formation of minerals with the existence of life on the Earth as in the rest of the Universe. Earth and Universe are not independent things. The natural inorganic world extends beyond the limits of the Earth as indicated by several authors by the relationship between the geological evolution and the phenomenon of life (Banfield et al., 1998; Amigó and Ochando, 2001; Bleeker, 2002; Hazen and Ferry, 2010). Therefore, geology, that is the study of Earth, represents only a small part of the natural inorganic world. As a first approximation, we can establish a relationship between astronomy and geology; both are sciences that are based on knowledge obtained principally from observation. Scientific knowledge developed from these astronomical and geological observations obtained by experimental methods and techniques can make predictions connected to the past, present and future observable events. Accordingly, we can establish an evolutionary view of the Universe and Earth to integrate all biological, geological, physical and chemical viewpoints. In this sense, the genesis of the Universe is related to the formation of our solar system and the evolution of life on our planet. The age of universe is about 15 billion years while humans only arrived about 3 million years ago (Mann and Weiss, 1996), on a planet whose absolute geological age appears to be about 4.5 billion years. This age has been determined from precise geochronology using isotopic dating methods.

Then I will endeavour to summarise the geological history of the Earth from the point of view of the evolution of the biological, physical and chemical processes that have given rise to the approximately 4,400 minerals recognized on our planet (Hazen, 2010). A mineral is a homogeneous solid, in nature typically formed by inorganic processes, which has an ordered atomic arrangement in a three dimensional space, and having a defined chemical composition (but generally not fixed, varying within certain limits). However, we know

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that the planet Earth is tectonically active, during which matter and energy interact with both outer space and with internal geological processes, resulting in plate tectonics (which interact to give rise the displacement and collision of continents causing earthquakes, volcanism and orogens), to the formation of natural resources (such as fossil fuels, rocks and minerals), and the origin and formation of life (arising from the interaction and evolution of the atmosphere and hydrosphere over the geological history of our planet as a result of complex biochemical reactions).

When the Earth formed, none of the more than 4400 minerals we know today existed (Hazen et al., 2008; Hazen, 2013). Cosmologists estimate that after 10 to -5, billion years following the Big Bang the first stars formed from the condensation of H and I (and probably some of Li), while the first elements were produced by melting processes (Schatz, 2010).

Only when giant stars transform into supernovas, nuclear reactions (nucleosynthesis) allow us to explain the observed abundances of chemical elements in the solar system and neighboring stars. These reactions (also called triple-?) take place over tens of millions of years and explain the formation of elements such as carbon and other with higher atomic number. Iron is the last stable element formed in this process. Therefore, diamond, graphite and SiC together with nitrides, oxides and silicates of magnesium should have been some of the mineral solid particles (nanometer-sized fan) being more abundant in planetesimals and interstellar matter condensation which gave rise to formation of first stars in the Universe (Clayton and Nittler, 2004). Perhaps for tens of millions of years were no more than a dozen of the unique mineral crystals in the Universe.

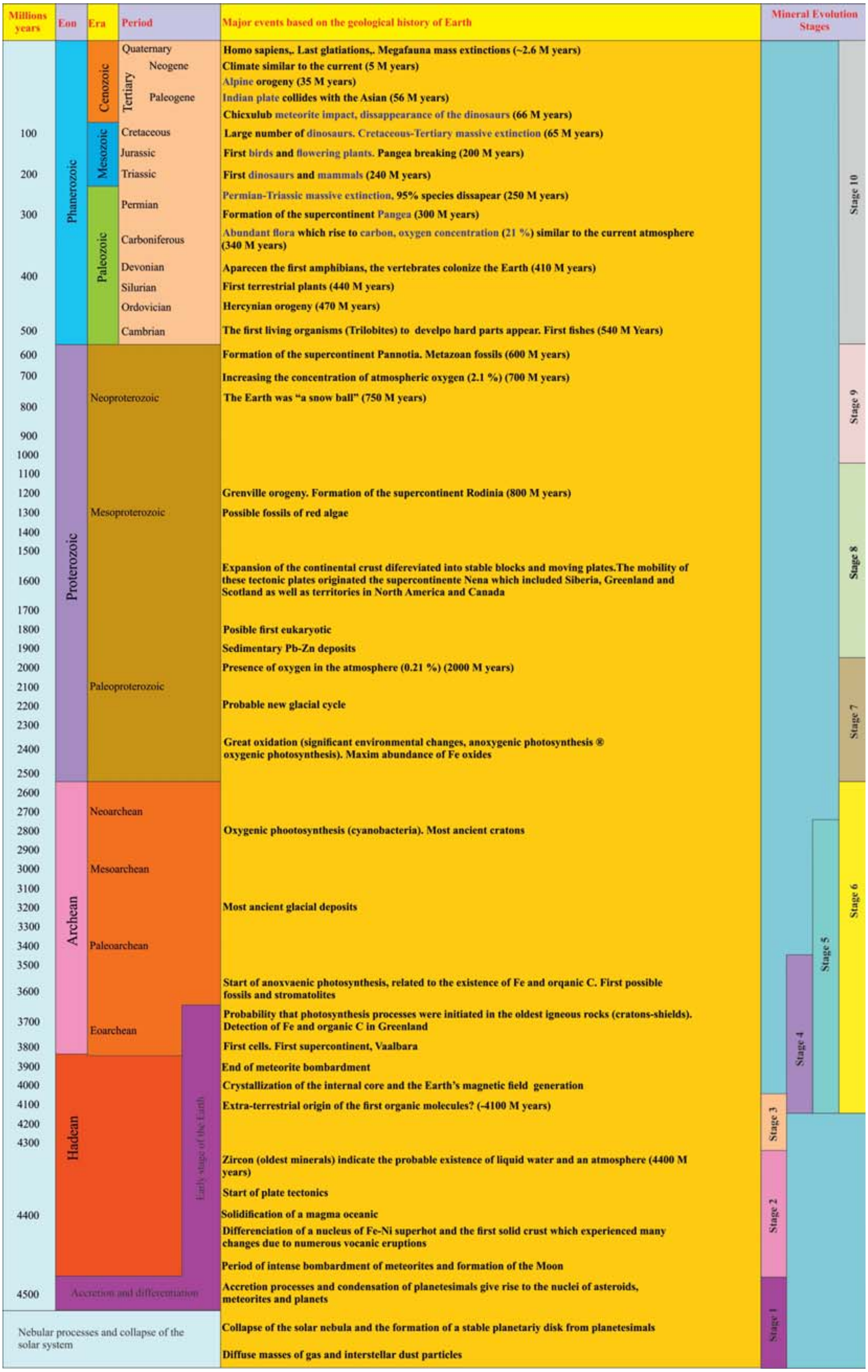
Starting from the formation of the solar system we can consider the following stages of biological, geological, physical and chemical differentiation affecting terrestrial minerals (Hazen et al., 2008):

- formed by accretion and differentiation of planetesimals in the presolar nebula;
- trained in primary geochemical differentiation of the Earth in an initial solid crust and a mantle-core cast undifferentiated;
- formed during the biogeochemistry evolution of Earth’s atmosphere.

2. The First Terrestrial Minerals: Interstellar Dust Particles (> 4.5 Ga)

Mineral evolution (Figure 1) began within a large cloud of interstellar gas and dust, called the solar nebula, which was formed by accretion and differentiation of planetesimals (interstellar dust) that further collided and accreted to form the terrestrial planets in the solar system. During this stage, before 4.5 billion years ago, the accretionary reactions of planetesimals, gave rise to the asteroids, from which comets and meteorites originate. Asteroids have a mineral composition simpler than our planet. The first minerals [Stage 1. Chondritic mineral formation (> 4.5 Ga)] formed by accretion at this stage are for the most part refractory components of chondritic meteorites (stony). Chondritic meteorites contain carbonaceous chondrules, spherical in shape and nanometric size, and characterised by the presence of organic compounds (a variety of hydrocarbons and amino acids) of unclear origin (Wood, 1967; Masuda et al, 1973; Richardson, 1978). Probably these compounds are not of biological origin, but their presence would be related to the organic compounds formed in the outer part of the solar nebula and the nuclei from which the meteorites originated. At this stage prior to the consolidation of the crust, a few dozen minerals, probably in a number about 60, were formed; many of them were of nanometer sized.

The Hadean Eon (term not recognized by the International Commission on Stratigraphy), which is the first division of the Precambrian period, corresponds to the time of Earth formation, some 4.6 billion years ago, and ends about 3.8 billion B.P., when the first crust was formed (Goldblatt et al., 2010). During this early stage the Earth was subjected to an intense bombardment of meteorites [Stage 2. Alteration, differentiation and planetisimals metamorphism (4.5-4.4 Ga), A decrease in the Earth’s temperature allowed the formation of mineral phases of low temperature (<100 °C) related to aqueous alteration of olivine and pyroxene to chlorite, serpentine, talc and other phyllosilicates as well as hydroxides, sulphates and carbonates. Also achondrite meteorites impacted as ferro-stone and siderite (composed of iron and nickel mainly) tending to modify the mineralogical composition of the Earth. The different types of stony achondrite meteorites represent the composition of the initial planetesimal crust of the Earth, with igneous mineralogical assemblage dominated by plagioclase and pyroxene. At this time, as a consequence of heavy meteorite bombardment that impacted on the Earth, some



Millions years	Eon	Era	Period	Major events based on the geological history of Earth	Mineral Evolution Stages
	Phanerozoic	Cenozoic	Quaternary	Homo sapiens,. Last glatiations,. Megafauna mass extinctions (~2.6 M years)	Stage 10
			Tertiary Neogene	Climate similar to the current (5 M years)	
				Alpine orogeny (35 M years)	
			Paleogene	Indian plate collides with the Asian (56 M years)	
				Chicxulub meteorite impact, dissappearance of the dinosaurs (66 M years)	
100		Mesozoic	Cretaceous	Large number of dinosaurs. Cretaceous-Tertiary massive extinction (65 M years)	
			Jurassic	First birds and flowering plants. Pangea breaking (200 M years)	
200			Triassic	First dinosaurs and mammals (240 M years)	
		Paleozoic	Permian	Permian-Triassic massive extinction, 95% species dissapear (250 M years)	
300				Formation of the supercontinent Pangea (300 M years)	
			Carboniferous	Abundant flora which rise to carbon, oxygen concentration (21 %) similar to the current atmosphere (340 M years)	
400			Devonian	Aparecen the first amphibians, the vertebrates colonize the Earth (410 M years)	
			Silurian	First terrestrial plants (440 M years)	
			Ordovician	Hercynian orogeny (470 M years)	
500			Cambrian	The first living organisms (Trilobites) to develpo hard parts appear. First fishes (540 M Years)	
600	Proterozoic			Formation of the supercontinent Pannotia. Metazoan fossils (600 M years)	Stage 9
700				Increasing the concentration of atmospheric oxygen (2.1 %) (700 M years)	
800		Neoproterozoic		The Earth was "a snow ball" (750 M years)	
900					
1000					
1100					Stage 8
1200				Grenville orogeny. Formation of the supercontinent Rodinia (800 M years)	
1300		Mesoproterozoic		Possible fossils of red algae	
1400					
1500					
1600				Expansion of the continental crust difereviated into stable blocks and moving plates.The mobility of these tectonic plates originated the supercontinente Nena which included Siberia, Greenland and Scotland as well as territories in North America and Canada	
1700					
1800				Posible first eukaryotic	
1900				Sedimentary Pb-Zn deposits	
2000				Presence of oxygen in the atmosphere (0.21 %) (2000 M years)	Stage 7
2100		Paleoproterozoic			
2200				Probable new glacial cycle	
2300					
2400				Great oxidation (significant environmental changes, anoxygenic photosynthesis ® oxygenic photosynthesis). Maxim abundance of Fe oxides	
2500					
2600	Archean				Stage 6
2700		Neoarchean			
2800				Oxygenic phootosynthesis (cyanobacteria). Most ancient cratons	Stage 5
2900					
3000		Mesoarchean			
3100					
3200				Most ancient glacial deposits	
3300					
3400		Paleoarchean			
3500					Stage 4
3600				Start of anoxvaenic photosynthesis, related to the existence of Fe and orqanic C. First possible fossils and stromatolites	
3700		Eoarchean	Early stage of the Earth	Probability that photosynthesis processes were initiated in the oldest igneous rocks (cratons-shields). Detection of Fe and organic C in Greenland	
3800				First cells. First supercontinent, Vaalbara	
3900	Hadean			End of meteorite bombardment	
4000				Crystallization of the internal core and the Earth's magnetic field generation	
4100				Extra-terrestrial origin of the first organic molecules? (-4100 M years)	Stage 3
4200					
4300					
				Zircon (oldest minerals) indicate the probable existence of liquid water and an atmosphere (4400 M years)	Stage 2
				Start of plate tectonics	
4400				Solidification of a magma oceanic	
				Differenciation of a nucleus of Fe-Ni superhot and the first solid crust which experienced many changes due to numerous vocanic eruptions	
				Period of intense bombardment of meteorites and formation of the Moon	
4500	Accretion and differentiation			Accretion processes and condensation of planetesimals give rise to the nuclei of asteroids, meteorites and planets	Stage 1
Nebular processes and collapse of the solar system				Collapse of the solar nebula and the formation of a stable planetariy disk from planetesimals	
				Diffuse masses of gas and interstellar dust particles	

Figure 1- Geological time scale that summarises the main geological events and the different stages of mineral developments, that have taken place on Earth (based partly on a schema of Hazen et al., 2008).

important minerals were formed (Hartman and Davis, 1975; Nickel, 1995; Nickel and Grice, 1998; Aspaug et al., 2011), which have become the main components of terrestrial rocks, such as quartz SiO_2, feldspar $KAlSi_3O_8$, titanite $CaTiSiO_3$, zircon $ZrSiO_4$ and others, formed by processes of hydrothermal alteration and metamorphism. In contrast, the Fe-Ni meteorites originated the planetesimal core, with dominant Fe-Ni alloys (kamacite, taenite) and metal sulfide [troilite FeS_2], carbides, graphite and phosphides [barringerite $(Fe, Ni)_2P$, schreibersite $(Fe,Ni)_3P$], which were the initial source of prebiotic phosphorus. Other phosphates, high-pressure phases of SiO_2 (coesite) and diamond are also associated with Fe-Ni meteorites. About 250 minerals were generated at the end of this stage (Figure 1).

3. The Earth Cools: Formation Of The Current Crust And Mantle (4.5-2.5 Ga)

Before the discovery that the composition of the Moon is the same as that of the Earth's surface, it was believed that composition of the Moon resembles to that of entire Earth. The impact of a large asteroid or protoplanet caused a cataclysmic collision (~ 4.6 Ga ago) which melted the crust and part of the outer mantle. This large collision affected the Earth, Moon and possibly the other four terrestrial planets. The surfaces of these planets favored the crystallization of igneous rocks, affecting the mineralogy of these rocks after meteorite and comet impacts over a long period of time. However, it is apparent that the balanced terrestrial mineralogy experienced many changes to the current structure. One of the probable causes is the existence of petrological, geochemical and geodynamic processes related with the plate tectonics, which affected both the crust and the mantle. Geologists have identified Hadean rocks in Greenland, Canada and Australia. Some zircons in Australian quartzites have been dated at about 4.4 Ga (Wilde et al., 2001), estimated age of formation of the Earth (Figure 1) [Stage 3. Initiation of the evolution of rocks (4.5-4.0 Ga)]. At this stage the igneous activity (magmatic differentiation; Bowen, 1956), favored terrestrial-rich volatile elements and facilitated the formation of large variety of volcanic and plutonic rocks. All these processes of diversification and mineralogy led to the formation atmosphere and hydrosphere (Cloud, 1968).

The components of this early atmosphere had to be N_2, CO_2 and H_2O, and H_2S, with minor amounts of CO, H_2, and CH_4. An immediate mineralogical consequence of the interaction with this atmosphere would be the formation of hydrated silicates (initial formation of clay minerals) and hydroxides. Also at this stage, the terrestrial poles are cooled to below freezing point, leading to the appearance of crystalline H_2O by the first time. Along this stage about 350 minerals could be funned.

At the boundary between the Hadean and Archean Eons [Stage 4. Granite formation and initiation of formation of cratons (4.0-3.5 Ga)], first cratons appeared which are composed of geological formations of internal continental masses, stable rock fragments containing primitive crust of the Earth, as well as remnants of the mantle-lithosphere evolution (Hamilton, 1999). This step of mineral evolution involves that the planet has a sufficient internal heat to melt the initial basaltic crust leading to the formation of granitoids or granitic rocks (Leake, 1990). Although the exact time of occurrence of these rocks is still uncertain, the formation of a continental granitic crust required several hundreds of millions of years (Figure 1). The evolution of granitoids led to the formation of pegmatites, which accumulated rare elements and Li, Be, B, Nb, Ta, U, among others, resulting in formation of about 500 minerals or more.

The detection of continental masses and possible volcanic phenomena indicates the existence of geodynamic movements such as displacement of plates and subduction related to what we now know as the plate tectonics [Stage 5. Start of the plate tectonics (>>3.0 Ga)]. The initial moment of these geodynamic processes is still under scientific debate (Rogers, 1996; Stern, 2007). To some a little before 4 Ga, most of this activity seems to be clear towards to 3 Ga (Fig. 1). Continental masses with ages of 3800 and 3500 million of years are the oldest dated rocks on the Earth. Also in this stage are recognized the first Cu-Pb-Zn sulphide hydrothermal deposits located in Australian Craton (3.5 Ga), Au and U detrital deposits in the African shield (2.9-2.7 Ga) as well as U in Canada (2.4 Ga). But many of these deposits are associated with metamorphic processes that have led to the formation of a number of minority phases, such as selenides, tellurides, arsenides, antimonides and other sulfosalts. Another consequence of plate tectonics is the formation of intermediate pressure minerals such as kyanite Al_3SiO_5, lawsonite $CaAl_2Si_2O_82H_2O$, glaucophane $Na_2(Fe,Mg,Mn)_3 AlSi_8O_{22}(OH)_2$, staurolite $(Fe,Mg)_2Al_9 (Si,Al)_4O_{20}(O,OH)_4$, and jadeite $NaAlSi_2O_6$. Although it is difficult to quantify the minerals at this stage of the Earth evolution, perhaps 150 additional new minerals and sulfosalts were generated by these geodynamic processes that took place in the crust and mantle.

In the Archean Eon which corresponds to beginning of biological life, the first bacteria appear to have been the origin of the formation of sedimentary Fe bands [hematite Fe_2O_3, magnetite $Fe^{2+} Fe^{3+}{}_2O_4$] and carbonate reefs. [siderite $FeCO_3$, dolomite $CaMg(CO_3)$, calcite $CaCO_3$,...] [Stage 6. Anoxygenic photosynthesis (3.9-2.5 Ga)] (Figure 1). Although the emerged land caused a pause in mineral evolution, weathering and the early life processes in these limited continental areas added 1500 new minerals. At this stage two groups of minerals, clays and transition metal sulfides, are normally considered.

4. Oxygen: The Molecule Of Life (2.5 Ga-Present)

Although there is no agreement (Lowenstam, 1981; Arrhenius, 2003; Parnell, 2004) on the origin of life, it requires a minimum of mineral evolution. There are different views on the origin of life on Earth. Some authors consider an exogenous or terrestrial origin, others consider that RNA first, then DNA and proteins at the end could have had an important role in the initial presence of life on Earth (Orgel, 1998).

The nature of the Earth's atmosphere changed in the Paleozoic Era when the concentration of oxygen in the Earth was increased (in the order of 0.1-0.2% of the actual concentration) [Stage 7. Great Oxidation (2.5-1.9 Ga)] (Fig. 1). This event begins with the increase of oxygen concentration by photosynthesis. This irreversible transformation of the Earth's atmosphere gradually changed the mineralogy of the Earth's surface (Bekker et al., 2004). At the beginning of this stage (~2.5-1.8 Ga), a great abundance (~ 90%) of Fe-Mn deposits of economic interest and other sedimentary minerals were formed [kutnohorite $Ca(Mn,Mg,Fe)\ (CO_3)_2$, pyrolusite MnO_2, rhodochrosite $MnCO_3$, rhodonite $(Mn,Fe,Ca)SiO_3$, riebeckite $Na_2Fe_5Si_8O_{22}(OH)_2$, chamosite $(Fe,Mg)_5\ (Al_2Si_3O_{10}(OH,O)_8$, chrysocolla $(Cu,Al)_2H_2SiO_5\ (OH)_4nH_2O$, turquoise $CuAl_6(PO_4)_4(OH)_84H_2O$, chalcan-thite $CuSO_45H_2O$, malachite $Cu_2(CO_3)(OH)_2$, azurite $Cu_3(CO_3)_2\ (OH)_2$, brochantite $Cu_4(SO_4)(OH)_6$]. Most of these minerals are associated with oxygenation by photosynthesis and oxidative weathering. More than 2500 minerals are hydrated, resulting from oxidative weathering of other minerals, although some were initially formed in anoxic environment (low in oxygen). The biochemical processes associated with the "Great Oxidation" event would be responsible, directly and indirectly, for the formation of the majority of currently existing 4400 minerals. For almost one million years there was no or limited mineral evolution (Holland, 2006). During this period, there was a clear separation between water layers in the ocean; more oxygenic surface layers and anoxygenic deeper layers [Stage 8. Ocean intermediate (1.9-1.0 Ga)]. At this period, sedimentary iron bands, which are characteristic of the Precambrian, abruptly cease indicating that the chemistry of oceans is greatly influenced by microbial activity and solar radiation. The transition from Paleoproterozoic to Mesoproterozoic indicates that mineralogical processes are very similar. There are no major mineralogical changes. We distinguish Pb-Zn sedimentary deposits in cratonic borders (~ 1.8 Ga), U deposits formed by weathering of granitic rocks in Canada and Australia (1.8-1.1 Ga) and sedimentary deposits of Cu in the center-southern Africa and Central Europe (1.4-0.2 Ga) (Figure 2) (Evans, 2013; Marschall et al., 2013).

The ninth stage of mineral evolution is characterized by major changes in climate and atmospheric composition. [Stage 9. Neoproterozoic glaciations (1.0-0.542 Ga)]. Some geologists have verified that towards the end of Proterozoic Eon, in rocks dated between 0.75 and 0.85 Ga, there are significant signs of glaciation. It seems that these glaciations affected all continents, in a way that the icy regions extended into tropical latitudes. What is still a geological debate is whether the surface of the seas and oceans froze completely, or almost completely (Figure 1). Volcanic activity continued at this stage, increasing CO_2 concentrations in the atmosphere, favoring the formation of aragonite. Also towards the end of this stage, the atmospheric oxygen concentration changes from <2% to ~ 15% of the current values which increases the formation of clay minerals on the surface of the continents (Kennedy et al., 2006) and the P concentration in seawater.

At the beginning of the Phanerozoic Eon biology dominates mineral evolution [Stage 10. Phanerozoic biomineralization (<0.542 Ga)]. The formation of nearly 60 minerals has been influenced by microbes, plants, invertebrates and vertebrates (humans included) (Figure 1). Accordingly, So in the Cambrian the first organisms are developed with hard parts. The mineral composition of these Cambrian skeletons are calcite and/or aragonite $CaCO_3$,

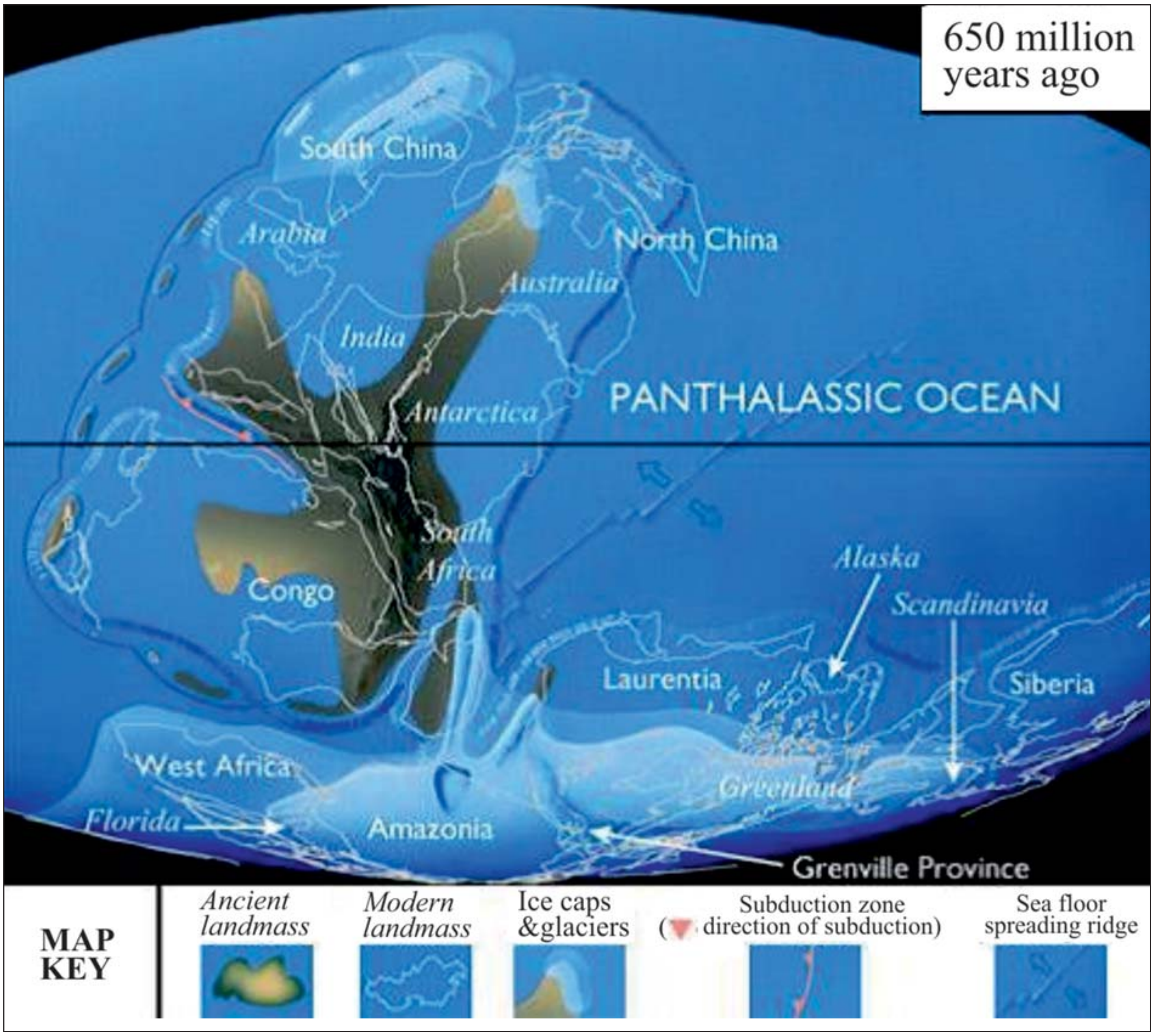


Figure 2- Rodinia, formed during the middle Proterozoic (~ 1100 million years), is the oldest supercontinent for which no record is available. (Evans, 2013; Marschall et al., 2013). Digitized by Principe Felipe Science Museum of Valencia.

magnesium calcite $(Mg_XCa_{1-X})CO_3$, apatite $Ca_5(PO_4)_3$ (Cl,F,OH) and opal $SiO_2{\cdot}nH_2O$. Calcium carbonates are, by volume, the most important biominerals as part of the hard parts of corals, molluscs and invertebrates (Stolarski et al., 2007). The calcite seems to dominate from the Cambrian to the beginning of the Carboniferous, but a sudden change to aragonite is observed towards the end of the Paleozoic to mid-Jurassic. These changes could be due to variations in the chemistry of the oceans, which could have facilitated the formation of skeletons with a mineral composition of magnesium calcite and aragonite. Phosphates are found in the skeletons of vertebrates (major minerals of teeth and bones) and invertebrates (e.g., in the shells of brachiopods). The precipitation of phosphates [hydroxyapatite $Ca_5(PO_4)_3$ $(OH)Ca_5$ and fluorapatite $Ca_5(PO_4)_3(F)$ principally] was facilitated by microorganisms present in the sea water, giving rise to formation of phosphor deposits currently exploited. During the Carboniferous large areas of forests were successively entombed giving rise to coal strata. Some scientists suggest that atmospheric oxygen concentrations in this period could be reached at ~35% (the current is 21%). The expansion of terrestrial vegetation, although did not alter the appearance of the land surface, has favored the formation of soils as well as clay mineral deposits that are exploited for ceramics and construction.

5. Conclusions

Minerals are commonly classified based on their chemistry (silicates, carbonates, halides, ..., according to the Dana's classification) or their crystallochemical character [Nesosilicates, cyclosilicates, inosilicates, phyllosilicates, tectosilicates, according to structural criteria established for silicates by Bragg (son)]. That is not normally related with terrestrial minerals within geodynamic history of the Earth. The geological history of mineral evolution is an interesting alternative to relate terrestrial mineralogy, as the extraterrestrial, with biology. It should be kept in mind that biology and geology are a part of the physical and natural sciences (Reventós et al., 2012), including biochemistry.

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