

Bauxites: Feedbacks of System Earth at Greenhouse times

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79-87 8 Figs. 1 Tab.

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ABSTRACT

The sedimentary record is an inexhaustible repository of information on global climates. The study of documents of past climate change may help us to understand not only the causes and presumable effects of the current change, but also to reveal the often complex and subtle mechanisms regulating the system. Ferrallitic soils and soil-derived sediments (=bauxites) are generally considered as best climate-indicators on dry-land. Their frequency distribution through geologic time shows pronounced positive anomalies coincident with greenhouse periods of Earth's history. It is proposed that intense ferrallitic weathering instead of being simply the passive product of the greenhouse could be also one of the negative feedbacks of the system counteracting warming by contributing to the pump-down of greenhouse gases from the atmosphere. In this way it helped to decelerate both the carbon-cycle and the hydrological-cycle. The mass-transfer of oxygen from the atmosphere to the lithosphere is tentatively considered as an additional negative feedback acting to slow down oxidative weathering on land. It is suggested that the study of bauxites and correlative anoxic sediments in the oceans should be used to reveal details of the above complex regulation mechanism.

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1. INTRODUCTION

More than 25 years ago, an IGCP Project - No. 287 „Tethyan Bauxites” - was initiated and enthusiastically joined by all the karst-bauxite geologists of the Mediterranean and beyond. Along with Prof. Goran Durn (then a student), his supervisor Prof. L. Palinkaš and the late Prof. Šinkovec, Prof. Jurković was among the participants sharing his experience and ideas about the geology and the bauxite deposits of the Dinarids. The main goal of that project was to summarize all published and unpublished data on Mediterranean karst bauxites in order to improve our understanding of the controls of bauxite genesis. At that point, tectonics was in the focus of interest, climate was taken for granted, inasmuch as humid tropical to subtropical conditions were considered as *causae sine qua non* of bauxite formation, providing the necessary geochemical environment of intense weathering. The localization of the deposits within the favourable climatic zone was assigned to geotectonic, geomorphologic and hydrologic factors and to the lithology of the karstic host rocks. That greenhouse conditions were of crucial importance in bringing about the anomalous abundance of bauxites in Cretaceous times was acknowledged by the community of IGCP-287 and tentatively exposed at EUG in Strasbourg 1991, then reiterated by D'ARGENIO & MINDSZENTY in their review on bauxites and palaeokarst in 1995. Major arguments for a causal relationship existing between the frequency distribution of bauxites and globally warm, humid climatic periods of the Earth history had perviously been put forward in 1982 by BÁRDOSSY, BÁRDOSSY & ALEVA (1990), D'ARGENIO & MINDSZENTY (1992) and FÖLLMI et al. (1993). Though there are also some doubts regarding the simplistic climatic interpretation of palaeoclays (eg. SINGER 1980;1984), or THIRY (2000), there is a general agreement about the anomalous abundance of bauxites in the stratigraphic record being

the signs of long-lasting warm-humid conditions in sub-erially exposed areas. The aim of the present paper is to show that instead of being passive products of the greenhouse, bauxites might have acted (though in a rather subtle way), as one of the feedbacks during the development and fading of the Cretaceous greenhouse.

2. BAUXITES - RELIABLE CLIMATE INDICATORS

The sedimentary record is an inexhaustible repository of information on global climates (eg. ERHART (1955, 1966, 1967), FRAKES (1979), PARRISH (1998) and many others). All the elementary processes of sedimentary rock formations, i.e. weathering, transportation, deposition even the early stages of diagenesis are, at least to some extent, climate-controlled. Mineralogy, chemistry, texture, structure of sedimentary rocks and their characteristic fossil assemblages being the direct or indirect results of climate-dependent elementary processes, may faithfully record past climatic parameters like temperature, humidity, evaporation, hydrogeochemistry etc. However, since climate is by far not the only factor determining the final appearance of a sedimentary rock, and since all postdepositional processes (including burial diagenesis) tend to conceal or at least to modify the original climate signal potentially preserved in sedimentary particles, there are but a few really reliable climate indicators.

A literature review of past climate changes may help to understand not only the causes and presumable effects of the current change, but they may also help to reveal the often complex and subtle mechanisms regulating the system. To pursue this goal it is useful first to review available data on modern climate-specific sediments such as evaporites, aeolian deposits, coral reefs and bauxites.

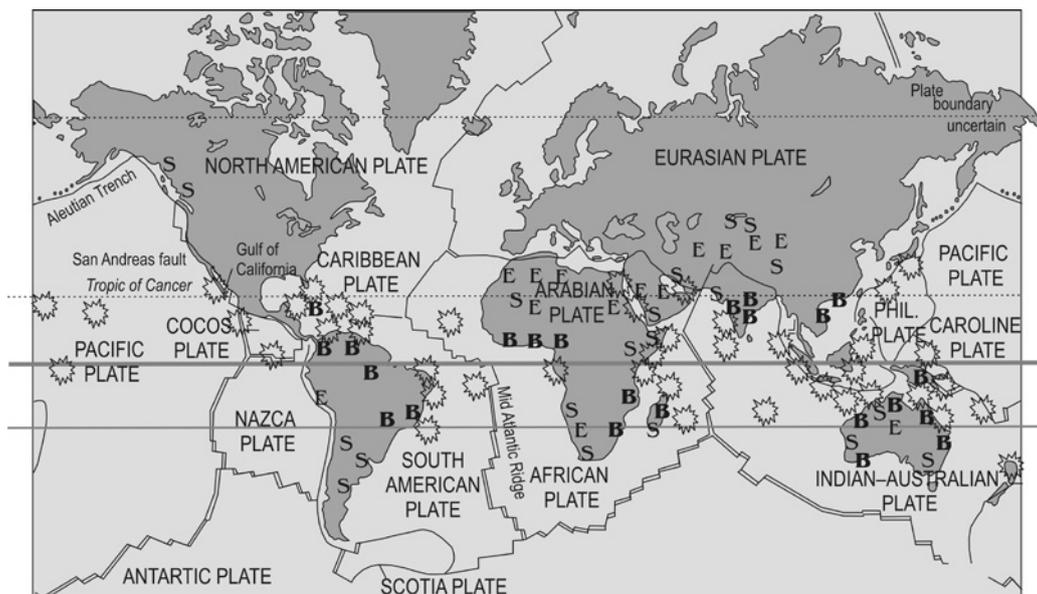


Figure 1. Global distribution of climate-dependent sediments (data from BÁRDOSSY & ALEVA, 1990, PARRISH 1998, SCOTESE, 2001). Legend: B=bauxites, S=evaporites, E=aeolian sands, asterisks=coral reefs

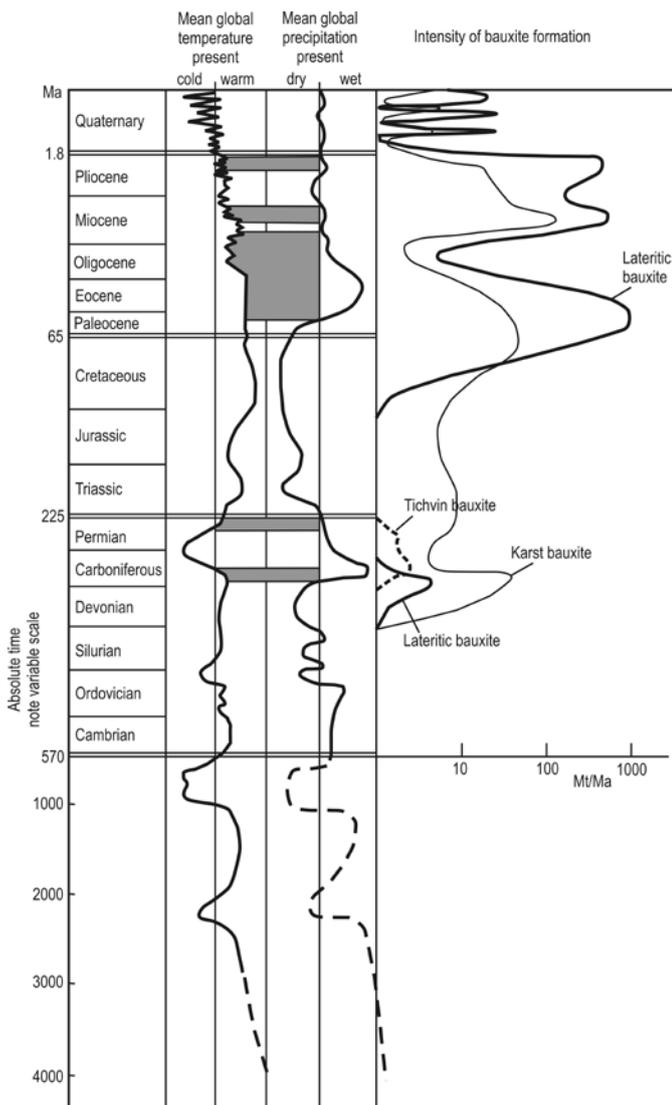


Figure 2. Relative abundance of bauxites in the stratigraphic record (after BÁRDOSSY & ALEVA 1990). (grey shading= warm wet periods)

Fig 1. shows the global distribution of modern climate indicators based on PARRISH et al. (1982), PARRISH (1998), BÁRDOSSY & ALEVA (1990) and SCOTESE (2001). Concise and also more sophisticated reviews are available in papers by PRICE et al. (1997a,b), SELLWOOD & PRICE (1994), ALLEN et al. (1994). They all confirm that in one way or another, all sediments are indeed climate-sensitive. There are two of them that seem to be properly restricted to one particular climatic zone, as *bauxites* and *coral reefs* occur exclusively in the tropics. In other words, in modern times, the best tropical climate indicators are coral reefs in the oceans and ferrallitic soils (oxisols i.e. equivalents of bauxites in the stratigraphic record) on dryland, and at least as far as ferrallitic soils are concerned, this must have been the situation throughout the Phanerozoic. The role of bauxites as unequivocal climate indicators has been confirmed by PRICE et al. (1997) and more recently by RETALLACK (2010). It has to be noted, though, that most bauxites, occurring on tropical landmasses, having been exposed since Mesozoic to Early Tertiary times, are not necessarily the products of the current climatic scenario (e.g, THIRY (2000) and others).

3. BAUXITES AND GREENHOUSE PERIODS

It was first pointed out by BÁRDOSSY (1982), then by BÁRDOSSY & ALEVA (1990), D'ARGENIO & MINDSZENTY (1992) and more recently by RETALLACK (2010) that the frequency distribution of bauxites through geological time shows pronounced positive anomalies coincident with the „greenhouse” periods of Earth history (Fig. 2). This trend is particularly well demonstrated by karst bauxites, the age of which is better constrained by the enclosing carbonates than that of those occurring in a lateritic association.

When, as an example focussing on Cretaceous karst bauxites and apparently contemporaneous global events, it is easy to see that even though the age-resolution of the studied phenomena is very different, bauxite-peaks are, indeed, coincident with *globally high temperatures*, concomittant *eustatic sea-level highs*, positive anomalies of *world-wide igneous activity* and

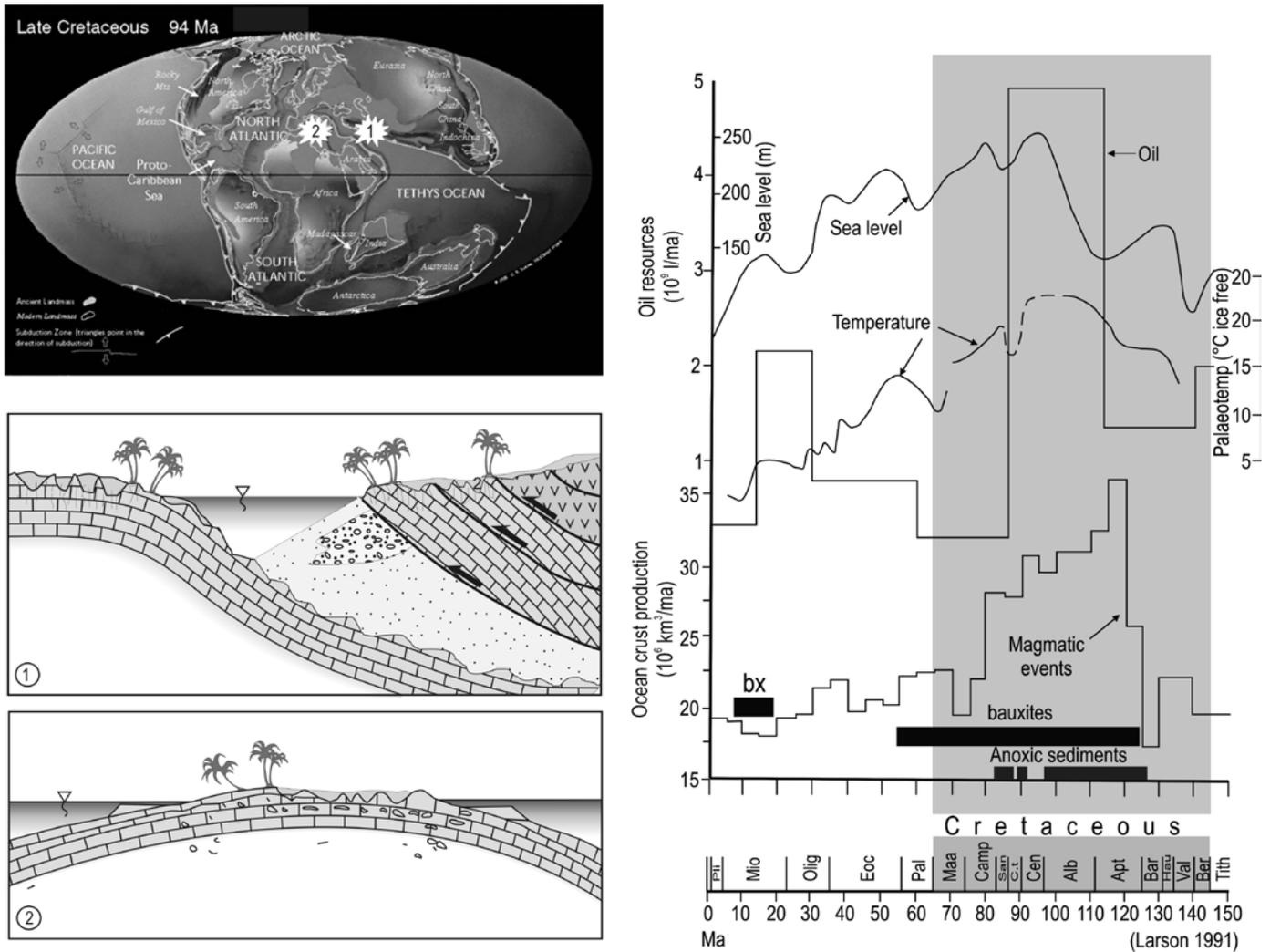


Figure 3. Cretaceous bauxites, geotectonics and paleoenvironmental factors (basic data from Scotese's PALEOMAP Project (2002), LARSON, 1990 and D'ARGENIO & MINDSZENTY (1994)) (white asterisks: position of the cartoons showing the geodynamic settings where bauxites occur).

abundant *oceanic anoxia* (Fig. 3). The correlation of bauxite-type weathering with peak global temperatures and sea-level may arise simply from the fact that all are direct consequences of the Cretaceous greenhouse. The correlation with the peak of igneous activity is certainly indirect, either because of the enhancement of atmospheric CO_2 and therefore a contribution to the greenhouse (LARSON (1991), LARSON & ERBA (1999), KURODA et al. (2007), which is also favourable for bauxites, or because of the release of large amounts of volcanic dust, providing the necessary source material for bauxites (MARIĆ, (1966); D'ARGENIO (1970); BÁRDOSSY et al. (1977); D'ARGENIO & MINDSZENTY, (1991, 1992).

It was this latter coincidence which at the time of IGCP-287 directed our attention to the relationship of bauxites and geodynamics, extensively discussed by BÁRDOSSY (1973), BÁRDOSSY & DERCOURT (1990), COMBES & BÁRDOSSY (1994), D'ARGENIO & MINDSZENTY (1991, 1995), MINDSZENTY et al. (1996). Peak abundance of Cretaceous bauxites in fact coincides with subduction and subsequent orogenic deformation all along the Alp-Himalayan orogenic belt.

The obvious reason for the *coincidence with orogenic deformation* is the requirement of exposed land for continental

weathering. At times of globally high sea-level as in Cretaceous times, the only way to provide for subaerial weathering (sufficiently long-lasting for bauxites to form) is the tectonically controlled uplift of large previously submarine areas. In fact, Cretaceous karst bauxites occur on tectonically affected shallow-water carbonate platform sectors all over the Tethyan realm and beyond (Figs. 3 and 4).

The correlation of bauxites with *oceanic anoxia* deserves special attention, because it connects two obviously climatically controlled, but seemingly unrelated, if not antagonistic phenomena: products of strongly oxidizing chemical weathering on land (which efficiently destroys/removes organic matter in/ from the soil, (e.g. PATEL-SORRENTINO et al. (2007) and oxygen-deficient, organic-rich sediments in the sea. Anoxic sediments form in places where the sediment surface intersects the oxygen-minimum zone of the oceanic water-mass. At greenhouse-times, when organic productivity is particularly high in the surface water-layer this may also happen in shallow shelf regions or else in partially closed compartments of the deep sea, where ventilation is insufficient to replace dissolved oxygen consumed by organic decay (Fig. 5) (e.g. SCHLANGER & JENKYN (1976); WEISSERT & MCKENZIE (1979); JENKYN (1980); and many others).



Figure 4. Areal distribution of Cretaceous bauxites. Base map from ZIEGLER (1988).

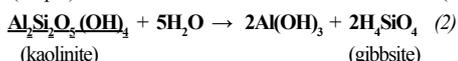
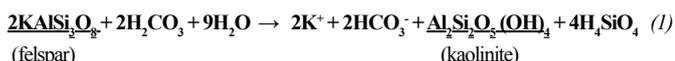
Key: 1 - continental crust, 2 - carbonate platforms/open shelves, 3 - pelagic/hemipelagic basins, 4 - terrigenous shelves, 5 - deformed belts and ophiolites, 6 - Oceanic crust and sediments, 7 - Tethyan karst bauxites (insert: world bauxites karst+laterite), AM - Armorican Massif, MC - Massif Central, BM - Bohemian Massif, EA - Eastern Alps, TR - Transdanubian Range, MP - Moesia, HE - Hellenids, HK - Dinaric High Karst, AP - Apulia, LA - Latium-Abruzzi, LC - Campania-Lucania, CS - Corsica-Sardinia, PY - Pyrenees, LP - Languedoc-Provence, IBM - Iberian Massif, 30° - estimated paleolatitudes (based on PARRISH et al., 1982, MÁRTON & MÁRTON, 1985 and SCLATER et al., 1977).

4. BAUXITES AND OCEANIC ANOXIC EVENTS – THE TERRESTRIAL AND THE OCEANIC CARBON PUMP

However unrelated those highly oxidized ferrallitic soils and anoxic sediments may seem to be, they may not only coincide in time but occur in close juxtaposition, as well.

This is particularly well demonstrated by the Dinaric-Adriatic-Apenninic domain in Cretaceous times (see Fig. 6), where bauxites on the exposed sectors of the Campania-Lucania, Abruzzi and Apulia carbonate platforms correlate very well with anoxic sediments in the Umbria-Marche Basin and in certain Adriatic shelf sectors (BÁRDOSSY et al. (1977); JENKYNS (1980); and Fig. 6).

When looking into the details of the geochemistry of anoxia and ferrallitic weathering both the apparent coincidence and the above juxtaposition may be explained.



Anoxic sedimentation in the oceans is considered as the essential part of the “biological carbon-pump” (eg. VOLK & HOFFERT (1985) in as much as CO₂ taken up from air/water by photosynthesizing organisms is efficiently transferred from the atmosphere to the lithosphere when dead phytoplankton reaches the ocean-bottom, becomes buried and thus withdrawn for a long time from the carbon cycle (cf. with JENKYNS (1980); SCHLANGER et al. (1987); and Fig. 5).

As pointed out by BERNER et al. (1983), BERNER (1991), AMIOTTE SUCHET & PROBST (1994), VELBEL (1993); LASAGA et al. (1994); and several others, chemical weathering also consumes CO₂ on land. So we may agree with BERNER et al. (1983), that in addition to the well-known *carbon-pump*, driven by *anoxic sedimentation* in the oceans, there is another, *land-based* (or terrestrial) *carbon-pump*, operated by chemical weathering likewise transferring carbon from the atmosphere into the lithosphere i.e. into soils and sediments. As shown by AMIOTTE SUCHET & PROBST (1994), more intense chemical weathering on the continents results in higher CO₂ consumption so periods with abundant ferrallitic soils (bauxites) may be signs of particularly efficient performance of the terrestrial carbon-pump.

The co-occurrence of the anomalous abundance of anoxic sediments and bauxites in Cretaceous times as pointed out by D’ARGENIO & MINDSZENTY (1992), FOELLM I et al. (1993), JENKYNS (2003) suggests that the two carbon pumps may somehow be coupled and when that happens, their effects may be greatly enhanced (Fig. 7).

Similar to Foellmi’s suggestion who, when explaining the anomalies of the Phosphorous-cycle, introduced the idea of the VITAMIN (Volcanically Induced Transfer and Accelerated Mineralization of Inhibiting Nutrients) periods (FOELLM I et al. (1993) and in agreement with JENKYNS (2003) who called attention to the increased amounts of continental runoff at times of peak greenhouse periods, we propose a Cretaceous scenario where nutrients (i.e. K, P, Ca, Mg, Na and also Fe) liberated by chemical weathering on land, reaching the ocean in solution by groundwater flow, and also by surface runoff (as fine hydrated particles) or as airborne dust, would significantly contribute to the increase of organic production in the photic

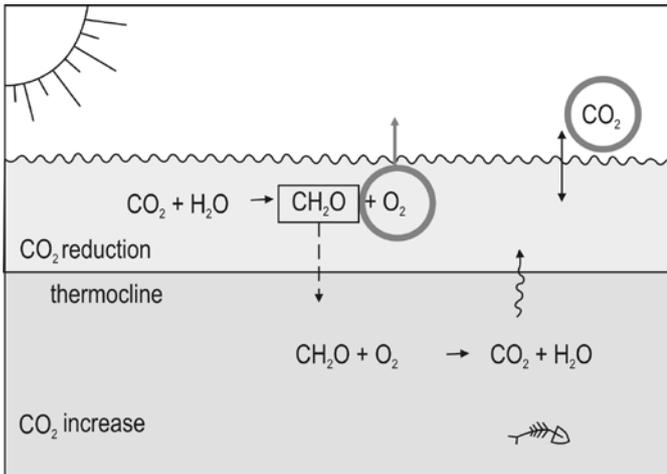


Figure 5. The oceanic carbon pump.

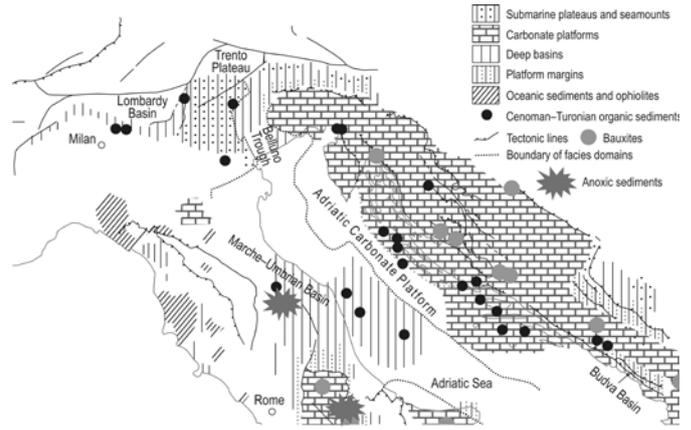


Figure 6. Areal distribution of bauxites and anoxic sediments in the Cretaceous of the Dinaride and Apennine sectors of the Mediterranean (base map and anoxic sediments from JENKYN, 1980).

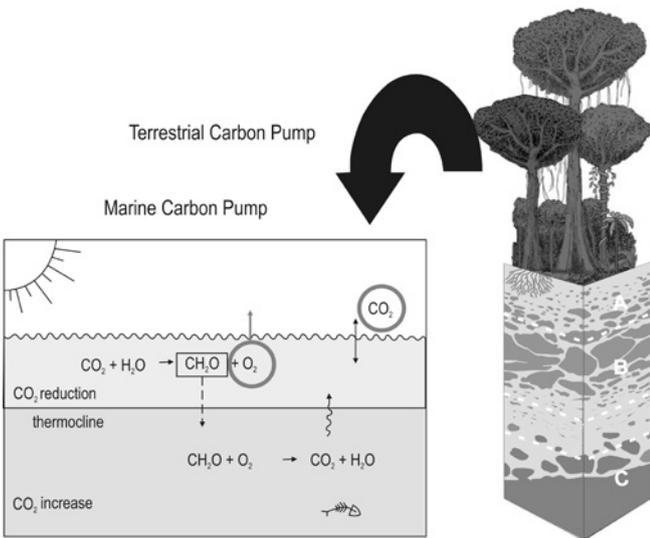


Figure 7. Coupling the terrestrial and the oceanic carbon pump.

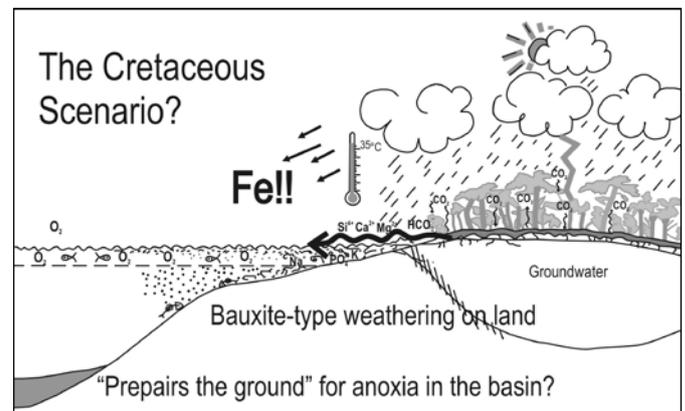


Figure 8. The Cretaceous Scenario with nutrients dissolved from the ferrallitic soil blanket and transported from the continent to the ocean as solutes by groundwater-flow and runoff and - as particulate material - by runoff and by wind.

zone (Fig. 8). In this way they may „prepare the ground” for anoxic sedimentation and thus trigger the withdrawal of excess carbon from the atmospheric reservoir. Calculations of LIU et al. (2010) for the recent world seem to support this idea even though they emphasize the need for further more detailed studies.

Among the nutrients introduced into the ocean, iron seems to play a rather particular role. The idea that Fe, being a limiting nutrient for organisms including eg. Chrysophyta and Bacillariophyta, is likely to be decisive from the point of view of the organic productivity of the oceans is more and more popular. As pointed out first by MARTIN & GORDON (1988) Fe-deficiency might result in zero productivity, even if all other conditions were favourable for life (=High Nutrient Low Chlorophyll areas). They suggested that in such low-productivity sectors of the oceans “iron-fertilization” would dramatically increase chlorophyll production. The hypothesis was tested in the late ‘80’s in the Pacific in the frames of the so called *IronEx* experiment (MARTIN & FITZWATER (1988). That dust may be blown out from tropical areas and carried all across the Atlantic by the trade winds as far as Bermuda was

previously detected by MUHS et al. (1990), and that South African dust may reach the South Indian ocean was shown by PIKETH et al. (2000). It was also shown that dust contains not only fine grained muscovite, feldspar and quartz but also abundant iron-rich alteration products (HERWITZ & MUHS (1995) or HERWITZ et al. (1996), etc.). That together with clay particles iron-rich particulate material may be introduced into the ocean by river runoff has also been known for a long time (e.g. CARROL (1958); POULTON & RAISWELL (2002). The possibility of natural iron-fertilization of the surface ocean by fine dust-related particulate Fe-oxides converted into bio-available iron by photochemical reactions was put forward by JOOS et al. (1991), TORTELL et al. (1999), GNANADESIKAN et al. (2003), JICKELLS et al. (2005), RIJKENBERG et al. (2005).

We have good reason to think that after long periods of particularly intense ferrallitic weathering on land (as at greenhouse times), when climate change begins and formerly humid areas gradually change for drier environments, rain forests give way at least partially to savannah type vegetation on the continents. As erosion is increased first by torrential

rains then by wind, the amount of river-born particulate iron and later on also of airborne ferrallitic dust may be increased and transported over the oceans, contributing to the increase in organic productivity of the surface waters. In this way, the performance of the marine carbon pump becomes greatly enhanced i.e. ferrallitic weathering on land helps to contribute to the slow-down of the carbon cycle. This „natural iron-fertilization” mechanism - as suggested also by MINDSZENTY & BÁRDOSSY in 2008 - would explain both the areal and temporal coincidence of bauxites and anoxic sediments at greenhouse times, i.e. also in the Cretaceous as proposed above.

5. BAUXITES, THE HYDROLOGICAL CYCLE AND THE COMPOSITION OF THE ATMOSPHERE

Molecular ratios of CO₂ and H₂O in the above simple equations (see (1) and (2)) suggest that when the end-product of ferrallitic weathering is bauxite (rich in gibbsite and goethite), weathering means efficient transfer not only of CO₂ but also of the greenhouse-„accelerator” H₂O from the atmosphere into the lithosphere. This is how it may contribute to the deceleration of not only the carbon cycle but also the water-cycle. At the same time ferrallitic weathering also consumes oxygen so in many ways it interferes with the composition of the atmosphere (cf with TARDY et al. (1989), BERGMAN et al. (2004), BERNER (2005)).

Oxygen is used in the oxidation of primary silicate minerals, organic matter and eventually pyrite. According to the calculations of COMBES & BÁRDOSSY (1995), the oxygen content of any weathered rock in the ferrallitic suite is, on the average, 10 % higher than that of its fresh parent material. Table 1. shows the relative amount of atmospheric oxygen fixed in Cretaceous ferrallitic weathering products, as calculated by Combes & Bárdossy.

As to the role of *water-vapour* in the atmosphere, there has been some debate among climatologists regarding its efficiency as a feedback mechanism amplifying/accelerating climate change when global warming has already begun SHERWOOD & MEYER (2006). Though the magnitude is still difficult to estimate, nowadays there is a general agreement, as a result of model simulations and satellite observations, that it works as a strongly positive feedback indeed (DESSLER & SHERWOOD, 2009).

When focussing our attention on the relative proportions of water molecules participating in the afore-mentioned equations (1), (2), the amount of water fixed in the alteration products is apparent at first glance.

Interestingly enough, unlike the role of silicate weathering in regulating the carbon-cycle previously discussed by BERNER et al. (1983), the possibility of hydrolithic i.e. ferrallitic weathering regulating the water-cycle (particularly when reaching the bauxite stage) has not been discussed by either of the available moisture budgets (eg. TARDY et al. (1989), TRENBERTH et al. (2006), LIU et al. (2010)).

A very simple minimum estimate of water chemically bound in Cretaceous ferrallitic weathering products can be attempted when taking into account the extent of continental areas for a Cretaceous palaeogeography (suggested as 20 502 x 10³ km² by TARDY et al. (1989) and calculating with only 10 metres of weathered material accumulated between 0 to 10 degrees latitudes N & S. This is an obvious underestimation since we know very well that in recent tropical areas ferrallitic weathering profiles may be several tens of metres thick, however they are mineralogically heterogeneous, so for the sake of simplicity it is easier to calculate here with a reduced thickness and with a homogeneous mineralogy as shown below). The average bulk density of the weathering product is taken as 2.4 g/cm³ (based on POSGAY (1967), BÁRDOSSY & ALEVA (1990) and HILL et al. (2006)). The amount of water chemically bound in such a 10 m thick weathered mantle can be calculated on the basis of the water-content of a 50-50% mixture of the two most abundant alumina minerals (gibbsite and boehmite) while the water bound in goethite and kaolinite is ignored at this point. This is again an oversimplification which may, however, be compensated for by the reduced thickness introduced above. Based on the data of HILL et al. (2006), and BROWN et al. (1953) for the water content of the alumina minerals (34.65 % for gibbsite and 15.02 % for boehmite), when calculating with an average water content of 24.84 weight percent, the resulting total amount of water chemically bound in ferrallitic weathering products of the Cretaceous world is 122.225x10³ km³. It is almost equivalent to the amount of water estimated by TRENBERTH et al. (2007) in their Global Water Budget recently stored as 122x10³ km³ „soil moisture” in the land reservoir and - regarding its order of magnitude - it is even comparable to the amount of water stored in lakes and rivers of the current land reservoir (178 x10³ km³).

Therefore, even this rough estimate calls attention to the role of hydrolithic weathering in the global water cycle. Continental runoff is, as a rule calculated by looking for the difference between the amounts of rainfall and evapotranspiration (eg. TARDY et al. (1989), sometimes also taking into consideration changes of soil moisture and groundwater (TRENBERTH et al., 2007)). However it is generally ignored that the part of what is

Table 1.

supposed intensity of weathering (m/Myr)	2 m/Myr	3 m/Myr	4 m/Myr	5 m/Myr
percent oxygen bound in bauxite (O _{x_{bx}} /O _{x_{atm}} x 0.1) (from Albian to Cenomanian, in 23 Myrs)	4.40%	6.50%	8.70%	10.90%
percent oxygen bound in bauxite (O _{x_{bx}} /O _{x_{atm}} x 0.1) (from Turonian to Senonian, in 26 Myrs)	4.50%	6.70%	8.90%	11.20%

Combes & Bárdossy (1995)

qualified as „runoff” is in fact transferred into the lithosphere and thus in the long run withdrawn from the water cycle.

It is suggested that over geological time scales the latter helps to remove not only carbon but also substantial amounts of water from the atmosphere. In other words: intense chemical weathering may substantially contribute to the slow down not only of the accelerated carbon-cycle but also the accelerated hydrological cycle.

In addition, ferrallitic weathering may counteract even one of the inherent positive feedbacks of greenhouse-warming, namely the production of CO₂ on oxidation of continental organic matter (peat). As pointed out above, COMBES & BÁRDOSSY (1995) suggested that the amount of oxygen bound in bauxites may be about 10 percent higher than in any of their fresh parent rocks. They calculated the quantity of oxygen bound in bauxites formed throughout Cenomanian and Turonian-Senonian times and compared the data to the quantity of atmospheric oxygen of each of those periods (as given by BUDYKO et al. (1987). They concluded that depending on the rate and the duration of the weathering process, about 4 to 11 percent of atmospheric oxygen may have become chemically bound to the alteration product, i.e. transferred from the atmospheric to the lithospheric reservoir. This is how ferrallitic weathering could have contributed to the decrease of the amount of free oxygen available for the oxidation of more terrestrial organic matter.

6. BAUXITES: POSITIVE OR NEGATIVE FEEDBACKS? - CONCLUSIONS

Even though their effect may be modest, it is suggested that in the long run, bauxites are undoubtedly one of the negative feedbacks: they release nutrients into the ocean (both via groundwater-flow and by air) and this way may help to intensify the oceanic carbon pump (i.e. contribute to the drawdown of CO₂ from the atmosphere). By chemically fixing part of the oxygen content of the atmosphere they may also help to decrease the rate of oxidation of terrestrial organic matter and thus slow down the rate of additional CO₂-release. By transferring H₂O into the lithospheric reservoir they may also help to decelerate the hydrological cycle.

To improve our understanding of System Earth, its controlling mechanisms and its feedbacks it is inevitable to look into the past and search for the documents of even minor feedbacks in the stratigraphic record. As the oceanic carbon-pump was recognized by looking into the details of anoxic sedimentation and its effects on the carbon-budget of the system (PREMOLI-SILVA et al. (1999), ERBA (2004) and others), it is very likely that additional, more detailed and quantitative study of bauxites may contribute to an improved understanding of the operation of the land-based H₂O (and carbon) pump as well. It is suggested that bauxites (palaeo-ferrallitic soils) were not only passive products of Phanerozoic greenhouse-episodes but they were parts of the feed-back loops helping the system to return to equilibrium after each large-scale greenhouse episode. This complies very well with the ideas of BERNER et al. (1983), FOELLMÍ et al. (1992), YUAN GAO et al. (2003) and RIDGEWELL et al. (2002) regarding the role of chemical weathering in controlling the carbon-budget of System Earth. Indeed, the comparative study

of bauxites, coeval anoxic sediments and modelled palaeo-wind trajectories (as in LINEN & HEATH (1981), would certainly disclose hitherto unknown details of this complex interaction.

Closing remark: After having submitted this manuscript I received a copy of the paper of LECHLER et al. (2015) in which the authors present convincing isotope-geochemical evidence for the importance of silicate weathering in sequestering atmospheric CO₂ during one of the Cretaceous Oceanic Anoxic Events (OAE 1a, Selli), so at least part of the theory seems to work also in practice.

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