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ΓΕΩΛΟΓΙΑ.— **Characteristic features of the Greek bauxites in view of their origin,** *by Dem. A. Kiskyras**. Ἀνεκοινώθη ὑπὸ τοῦ Ἀκαδημαϊκοῦ κ. Λουκᾶ Μούσουλου.

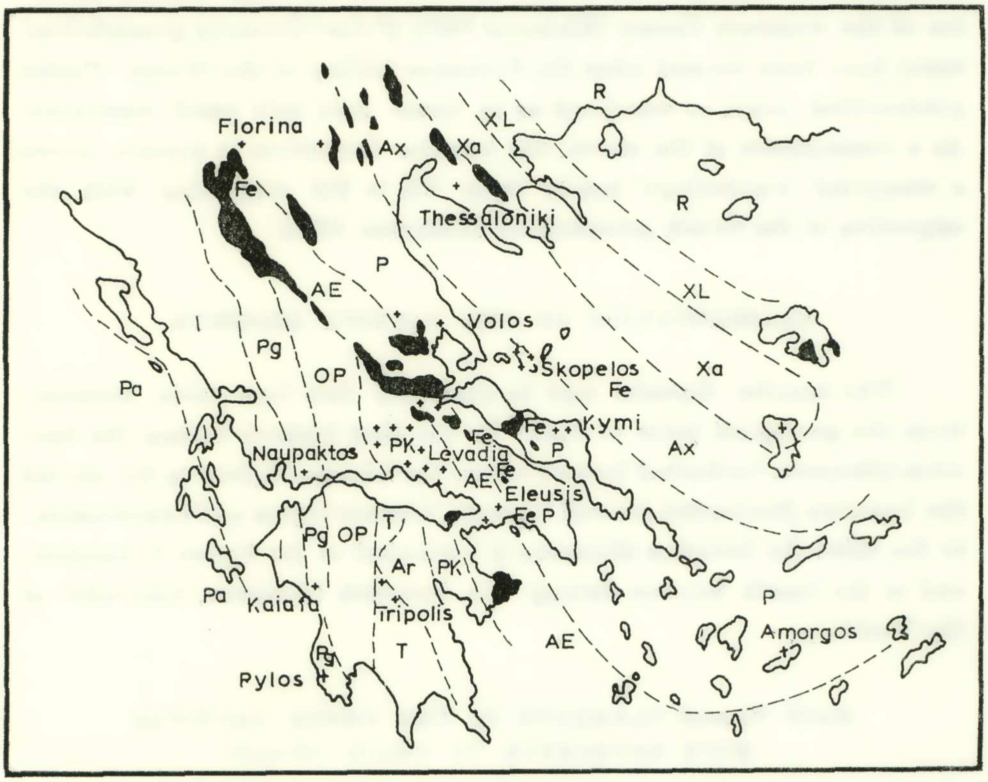
ABSTRACT

The Greek bauxite deposits were laid down from Jurassic to Eocene; earliest to latest deposition was from NE to SW respectively. Their formation is connected with a regression associated with a strong karstification of neritic carbonate deposits unconsolidated upon emergence from the sea, which took place under physico-chemical conditions involving the deposition of bitumenous limestones in the proximate shallow sea. Bauxites genetically associated with igneous rocks are very rare in Greece, and occur in small and unimportant deposits with a high SiO_2-content, making these deposits uncommercial.

FAVOURABLE PERIODS FOR BAUXITE FORMATION

The Greek bauxites from the genetic point of view are characterized by the occurrence of deposits interbedded with neritic carbonate rocks in a geoanticlinal zone. Their formation coincides with the sedimentation break due to a regression associated with orogenetic movements displayed in a geosynclinal zone east of it (Kiskyras 1972). Thus, the Jura-

* ΔΗΜ. Α. ΚΙΣΚΥΡΑ, **Χαρακτηριστικὰ γνωρίσματα τῶν ἑλληνικῶν βωξιτῶν σὲ συσχετισμὸ μὲ τὴν προέλευσή τους.**



Black blots = Ophiolites
+ = Bauxite
Fe = Cr-Ni-Fe Ores
Pa = Pre-Apulian zone
T = Tripolis zone
I = Ionian zone
PK = Parnassos-Ghiona zone
Pg = Pylos-Gavrovo zone
AE = Eastern Hellenic zone
OP = Olonos-Pindos zone
Xa = Chalkidiki zone
P = Pelagonian zone
XL = Eastern Chalk. Lesbos zone
Ax = Axios zone
R = Rodope zone

Fig. 1.

ssic, Lower Cretaceous and Upper Cretaceous bauxites are connected with regressions following the late Cimmerian, the Austrian and the Subhercynian folding respectively. In the same way, the Eocene bauxites of the weastern Greece (Kiskyras 1958) (Pylos - Gavrovo geoanticlinal zone) have been formed after the Pyrenean folding of the Olonos - Pindos geosynclinal zone, so restricted as to cause here only small emersions. As a consequence of the above, the bauxite formation in Greece shows a «temporal wandering» nearly from NE to SW coinsiding with the migration of the Greek geosynclines (Kiskyras 1980).

CLASSIFICATION OF THE BAUXITE DEPOSITS

The bauxite deposits may be classified into four main horizons, from the geological point of view. To the first horizon belong the bauxites (diaspore, boehmite) formed before the Kimmeridgian ; to the second the bauxites (boehmite) formed between Kimmeridgian and Cenomanian ; to the third the bauxites (diaspore + boehmite) of the Upper Cretaceous, and to the fourth horizon belong the bauxites (diaspore, boehmite) of the Tertiary.

MAIN TRACE ELEMENTS IN THE GREEK BAUXITES WITH REFERENCE TO THEIR ORIGIN

Some bauxites contain chromium and nickel in high values so that the ophiolites of the eastern Hellenic zone are considered to be their source rocks (Aronis 1954, Aronis and Roch 1958, Papastamatiou 1962, Bardossy and Mack 1967, Nia 1968, etc.). With respect to the Eocene bauxites of the western Greece, it was supposed (Kiskyras 1962) that they are not derived from igneous rocks but rather from limestones and dolomites. In the Mandra (near Athens) deposit, only about $^1/_4$ of the bauxite originated in lateritized ultramafic rocks, and the essential source of alumina was probably the lateritized schists (Papastamatiou and Maksimomič 1969). The view that the schists have been an important source for the bauxite formation was later supported by other authors (Augustithis et al., 1978).

The opinion that the Greek bauxites are derived from the ophiolites of the eastern Hellenic zone may be proved correct only for the Upper Cretaceous bauxites, because the Jurassic and the Lower Cretaceous bauxites arose before the laterization of the mentioned ophiolites. Tab. I shows that the Cr-content of the Upper Cretaceous bauxites is greater than the Cr-content of the Jurassic and the Lower Cretaceous bauxites. Still greater is the Cr-content in the Mandra bauxite deposit, 16 km distant from ophiolites, but far greater is the Cr-content in the Makrykapa (Euboea) bauxite situated in the vicinity of the ophiolites. The high Cr-content of the Upper Cretaceous bauxites doubtleesly indicates that their chemical contents has been influenced by the laterization of ophiolites.

It may be added that the deposits of the third bauxite horizon are closer together than the deposits of the other horizons, yet, moreover their regional distribution is very wide so as to cover some deposits of the other bauxite horizons. But all this does not mean that the Upper Cretaceous bauxites were derived directly from the ophiolites. It is well known (Kiskyras 1978) that the footwall limestones of these bauxites contain ophiolite fragments and, moreover, all the trace elements established in bauxites are present in the limestones. Therefore, the opinion has been expressed (Kiskyras 1978) that the Greek bauxites of economic interest have been derived from limestones and dolomites, contaminated during their sedimentaion with ophiolite fragments.

Bauxite source rocks were early considered to be the only alumina rich rocks; yet, the ability or capacity for rocks to weather is more important for bauxite formation than their alumina content. The limestones and calciferous sandstones undergo weathering (dissolution) more readily than other rocks. The residual products of limestone karstification is often less than 1 %. Such was the more important objection to the theory that limestones should be the source rocks of the bauxite. The bauxite does not cover the entire surface of the limestone area but only a small part of it, about $^1/_{50}$ (Kiskyras 1978). That bauxite has been formed by the accumulation of residual products may be taken the 50 fold Al-content of the limestone for the correct relation between Al-content of bauxite and that of limestone.

TABLE I

Chromium and Titanium content in bauxites.

Deposits	Cr%	Ti	$\frac{Fe_2O_3}{TiO_2}$	$\frac{Al_2O_3}{TiO_2}$	Fe/Cr	Al/Cr	Everage of
Jurassic Bauxites.......	0.031	1.52	8.67	22.3	469.22	942.20	57 analyses
Upper Cretaceous Bauxites far from ophiolites.....	0.159	1.58	9.12	21.32	165.43	305.02	62 »
Upper Cretaceous Bauxites 16 km far from ophiolites.	0.217	1.34	16.28	21.82	119.42	239.39	7 »
Upper Cretaceous Bauxites near ophiolites	0.736	1.45	14.89	20.57	32.98	38.28	4 »
Cr-Ni-Fe Ores in the east. Hell. Zone	1.41	0.37	76.55	14.96	18 25	3.56	44 »
Eocene Bauxites in the W. Greece............	0.255	1.69	7.55	18.07	53.03	121.90	12 »

RELATIONSHIP BETWEEN LIMESTONE FACIES AND BAUXITE FORMATION

a. Main bauxite layers.

For the association of the bauxite formation with a regression over limestone, let us suppose that the karstification of carbonates involves young unconsolidated marine carbonates as with the Jamaica bauxite (de Weisse 1977). In such cases the weathering and the dissolution of carbonates proceeds rapidly and easily. The question here is always of neritic and never of pelagic limestones. If the Greek bauxites had been directly derived from ophiolites, they should be found also over pelagic limestones emerged before the deposition of the bauxite material. It is of interest to note here that bauxite and hanging wall limestone are deposited throughout on karst depressions (dolinas). This indicates that an intensive karstification took place here before the deposition of the bauxitic material, i.e. a close relation of the bauxite formation to the landward karstification. (The bauxite formed from the residual products of the karstification). Otherwise we cannot explain disappearance of the huge volumes of residual products. The absense of any angular unconformity of the hanging — with the foot — wall may be explained in this way.

The deposition of the bauxitic material was followed by a feeble transgression associated with the formation of shallow neritic bituminеous limestones. The Eocene bauxite of Klokova (Weastern Greece) is overlain by a thin lignite layer. The hanging wall of the third bauxite horizon of the Parnassos - Ghiona zone consists of brownish black bituminous limestone of the Upper Cretaceous while the footwall consists of a whitish grey nonbituminous limestone of the Cenomanian. It is noteworthy that the hanging wall of the Mandra bauxite consists also of a Cenomanian limestone but dark brown coloured, and bituminous. Such would indicate that two limestone facies appeared during the Cenomanian in the Greek area. The darkest first formed at the end of the bauxite formation of the second horizon; the other, the white, ended at the begining of the third bauxite horizon formation.

b. Satellite — and intercalary — bauxite layers.

Another bauxite layer often appears, but this in the hanging wall of the second bauxite horizon, inserted in its lower part. This bauxite layer, called Satellite layer, occurs in lenses and ranges, according to the karst topography of its footwall, from a few meters to several tens of meters in lenght and from 0.3 to 9.0 m. in thickness, sometimes two or more satellite lenses are present over the main bauxite layer. The thickness of intermediate limestone is very small and varies from 0.3 to 5.0 m. This may be attributed to the short transgression in this district after the bauxite formation on the one hand, and to the strong karstification of the more recently deposited and unconsolidated, emerged limestone on the other hand, followed by a new bauxite formation, also in shape of pocket deposits. Both, main and satellite layer, have the same mineralogical composition (boehmite, hematite, kaolinite, diaspore, anatase and rutile) which means that the bauxite formation conditions did not change during the second regression in this district. This regression may be considered as a pulse of the late phases of the young Cimmerian folding taken place in the internal Hellenic zones. The question here is of a feeble regression because the satellite layers occur in places, corresponding to the marginal parts of the karst depression, where the main bauxite layer is thin. It may be noticed that no satellite layers are known in places with a thick bauxite layer. The main bauxite layer is often thicker and of better quality, i. e. rich in Al_2O_3 and poor in SiO_2, than the satellite layer, but sometimes the opposite occurs.

Fig. 2 and 3 show some satellite bauxite layers in the deposit of the second horizon Peristera, situated about 4 km south of Distomon. Such a satellite layers are known from the deposit Sklivinitsa NW of Distomon, from the Tourbatsi deposit E of Distomon and from the Spareika Mandria deposit SE of Distomon.

Bauxite lenses of small dimensions are rarely been intercalated in the upper parts of the third horizon foot wall, i. e. the upper parts of second horizon hanging wall, f. i. in the third horizon deposit Agios Konstantinos, situated about 1 km south of Distomon. These bauxitic lenses may be called intercalary layers in order to be distin-

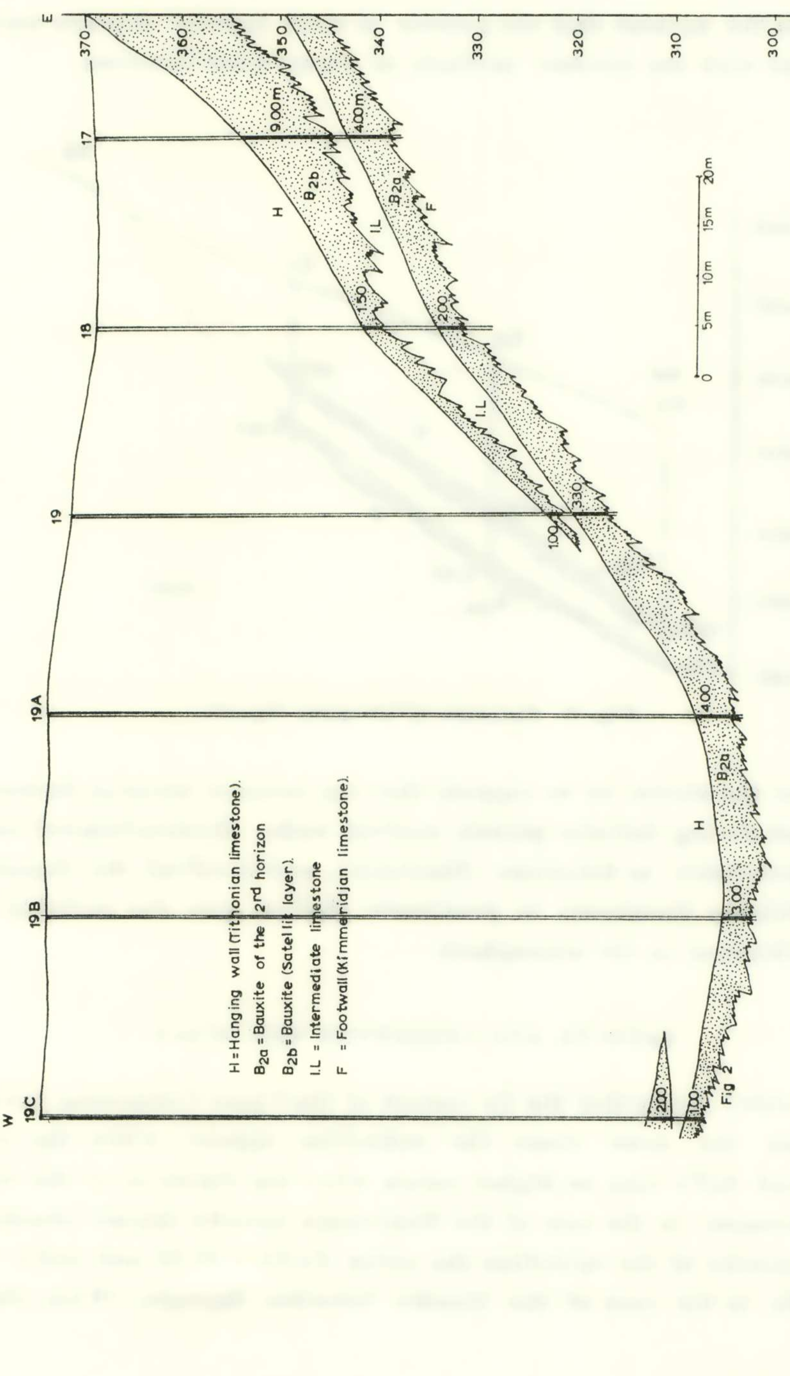


Fig. 2. Section though the bauxite deposit Peristera (Distomon).

guished from the satellite layers. Their formation may be connected with a pulse of the Austrian phase of the Alpine orogeny in this area.

The occurrence of the satellite bauxite layers, mentioned above, favorates the opinion that the genesis of some bauxite deposits may be associated with the residual products of strong karstifications.

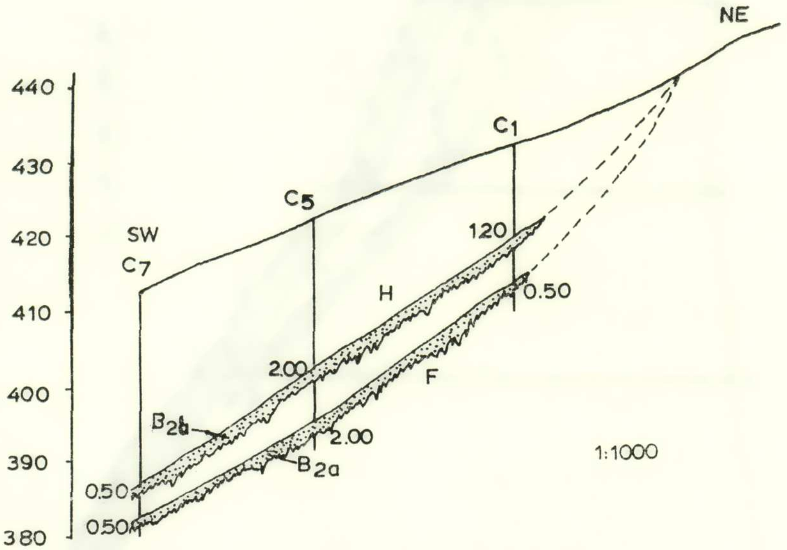


Fig. 3. Peristera (Distomon) deposit.

For the above, let us suppose that the bauxitic material formation, restricted during definite periods evolved under physicochemical conditions favourable to limestone dissolution, and involved the deposition of bituminous limestones in proximate, shallow seas, due probably to a CO_2-enrichment in the atmosphere.

BAUXITE AND LIMESTONE RESIDUALS

Table I shows that the Cr-content of the Upper Cretaceous bauxites increases the more closer the ophiolites appear, while the ratios Fe/Cr and Al/Cr take on higher values when the distances of the ophiolites increases. In the case of the Makrykapa bauxite deposit situated in the proximity of the ophiolites the ratios Fe/Cr = 32,98 and Al/Cr = 38, 28, while in the case of the Mandra bauxites deposits, 16 km distant from the ophiolites, the values of the ratios Fe/Cr and Al/Cr increase to 119.42 and to 239.39 respectively. With regard to the other bauxite deposits, more remote from ophiolites, the values of the ratios Fe/Cr and Al/Cr increase still more but no correspondingly with the distance from the ophiolites.

This indicates that the chemical composition of the bauxite was under the influence of the ophiolites up to a distance, where the mechanical transport of the ophiolitic material is conceivable possible. This explains why the Greek bauxite deposits do not show any preference for arrangement on the side of the ophiolites of the eastern Hellenic zone. They appear, often, so relative to the footwall limestones that the contact of the footwall with the hanging wall is mapped as a closed line. This regional distribution of the Greek bauxite deposits favours the view that the mentioned bauxites have been formed by accumulation of karstification residual products.

It should be very interesting to note that the Eocene bauxites situated (Fig. 1) further from ophiolites than all the other bauxites present a high chromium and titanium content. The mean values Fe/Cr = 53.03 and Al/Cr = 121.9 are very small, so it might be said that they correspond to short distance transportation of chromium and, consequently, to a bauxite formed not far from the source rocks. But, since in this area no other rocks other than limestone are present, it is considered and indicated that the limestone is the source rock. When the decalcification took place in an alkalizing environment the residual material was enriched with Al_2O_3, and bauxite was formed. On the other hand, in oxidizing environment, the Fe_2O_3-enrichment was greater with resulting iron oxide, the chemical composition of which is given in the following analysis (KISKYRAS 1962):

L.o. Ign	SiO_2	Fe_2O_3	TiO_2	CaO	Al_2O_3
6.15%	5.93	78.79	0.51	1.35	7.22

The location of bauxite directly above iron oxide will be explained by a change of the physico - chemical conditions in the environment. The question here is of a feeble transgression resulting in a shallow sea bottom.

Some bauxite deposits situated near the source rocks are rich in Fe_2O_3, while others laying far from these have been enriched with Al_2O_3 for the reason that iron, here as Fe^{2+} with lower ionic potential, still remains in solution.

It may also be mentioned that the amount of titanium is greater in bauxites than in Cr-Ni-Fe ores in the eastern Hellenic zone, originating from ophiolites, which are especially titaniferous rocks. This implies that the Ti-enrichment of the bauxitic material increases with increasing distance from the source rocks. However, the Al_2O_3 enrichment increases more rapidly than the TiO_2 enrichment, with the ratio, Al_2O_3 / TiO_2, higher values with increasing distance from the source rock. Thereafter, it may be assumed that the Eocene bauxites with their low values of the ratio Al_2O_3/TiO_2, do not lay far from the source rock.

This may be attributed to the higher ionic potential of titanium ($I = 5,9$) in comparison with that of aluminium ($I = 5,3$) causing earlier its precipitation. So, bauxites can be characterized by their Al- and Ti-enrichement, while the lateritic iron ores bu an Fe- and Cr-enrichment. The Ni-enrichment of the iron ores took place later, after their deposition, and regards especially the deeper parts of the deposits. The question here is of a secondary enrichment, due to the fact that nickel with small ionic potential ($I = 2,6$) is more movable than Cr^{3+}, Ti^{4+} and Fe^{3+}, and reaches the lower parts of the iron deposits, in proportion to their orientation relatively to the local surface morphology. Such a secondary enrichment with nickel sometimes occurs in bauxite deposits, as in the case of the Marmara - Megaron deposit (de Weisse 1967) situated near to ophiolites. An other paper will soon report of a similar enrichment, but with iron, of the bauxite deposits lower parts.

BAUXITES GENETICALLY ASSOCIATED WITH IGNEOUS ROCKS

Also in Greece are bauxites genetically associated with igneous rocks but they are very rare, and they occur in small and unimportant deposits. As such, the SiO_2 content in these bauxites is too high making the bauxites uncommercial. The Al_2O_3 content in these bauxites does not show a regular dependance on the Fe_2O_3 - content but it changes irregularly as in the case of the Cr-Ni-Fe ores. With respect to the other bauxites, the Al_2O_3 - content increases regularly with decrease in Fe_2O_3, with the exception of the bauxites in deposits, where a strong deferrification of the upper parts and a referrification of the lower parts took place. Sometimes a bauxite associated genetically with igneous rocks is later underlain by an other bauxite of limestone origin. This concerns the Arpini (Lamia) deposit. This rose coloured bauxite ($SiO_2 = 25{,}49\,\%$) contains disintegrated feldspars, pyroxene and illite.

The question, as to whether a bauxite originates in limestones or in ingneous rocks has scientific as well as economic interest. In the first case, there are chances to discover bauxite below neritic limestones. In the second case, the hope for finding bauxite is very restricted because the igneous rocks are very sparse in the geoanticlinal zones and the bauxitic materials do not originate at great distances.

ΠΕΡΙΛΗΨΗ

Οἱ συνθῆκες σχηματισμοῦ τῶν ἑλληνικῶν βωξιτῶν παρουσιάζουν μιὰ χρονικὴ μετανάστευση ἀπὸ τὸ Ἰουρασικὸ πρὸς τὸ Ἠώκαινο μὲ κατεύθυνση περίπου ἀπὸ ΒΑ πρὸς ΝΔ, ὅπως ἔγινε καὶ μὲ τὴν ὡρίμανση τῶν ἀλπικῶν γεωσυγκλίνων στὸν ἑλληνικὸ χῶρο. Ἡ γένεση τῶν βωξιτῶν συνέπεσε μὲ περιόδους, ὅπου ἔγιναν ἀποχωρήσεις τῆς θάλασσας σὲ γεωαντικλινεῖς ζῶνες καὶ ἔντονη καρστοποίηση ἀνθρακικῶν πετρωμάτων, ποὺ μόλις εἶχαν ἀναδυθεῖ ἀπὸ ξέβαθη θάλασσα, χωρὶς νὰ ἔχουν ὑποστεῖ συμπαγοποίηση, ἐνῶ σὲ γειτονικὲς ξέβαθες θάλασσες σχηματίζονταν βιτουμενιοῦχοι ἀσβεστόλιθοι. Τὰ ὑπόλοιπα ἀπὸ τὴν καρστοποίηση ἐμπλουτίσθηκαν σὲ Al_2O_3 καὶ TiO_2 τόσο κατὰ τὴν ὑδάτινη μεταφορά τους, ὅσο καὶ κατὰ τὴν ἀπόθεσή τους σὲ ἀλκαλικὸ περιβάλλον. Ἀπὸ τὰ ὑλικά, ποὺ ἀποτέθηκαν κοντὰ στὰ μητρικὰ πετρώματα, σχηματίσθηκαν βωξῖτες πλούσιοι σὲ τρισθενῆ σίδηρο, ποὺ κατακρημνίσθηκε ἐνωρὶς ἀπὸ τὶς διαλύσεις, ἐνῶ σὲ μακρυνότερες ἀποστάσεις σχηματίσθηκαν βωξῖτες πτωχοὶ σὲ σίδηρο, διότι τὸ ὑπόλοιπο τοῦ σιδήρου, ποὺ ἦταν σὲ δισθενῆ μορφὴ μποροῦσε, λόγω τοῦ μικροῦ ἰοντικοῦ δυναμικοῦ, νὰ μεταφερθεῖ σὲ μεγαλύτερες ἀποστάσεις.

Οἱ βωξῖτες μποροῦν νὰ χαρακτηρισθοῦν σὰν λατεριτικὰ μεταλλεύματα, ποὺ ἐμπλουτίσθηκαν μὲ ἀργίλιο καὶ τιτάνιο, ἐνῶ τὰ λατεριτικὰ σιδηρομεταλλεύματα ἐμπλουτίσθηκαν σὲ σίδηρο καὶ χρώμιο. Ὁ ἐμπλουτισμὸς αὐτῶν σὲ νικέλιο ἔγινε ἀργότερα (δευτερογενὴς) καὶ παρουσιάζεται ἰδιαίτερα στὰ χαμηλότερα τμήματα τοῦ κοιτάσματος καὶ μάλιστα ἀνάλογα μὲ τὸν προσανατολισμό τους σχετικὰ μὲ

τὴν τοπικὴ ἐπιφανειακὴ μορφολογία. Παρόμοιος δευτερογενὴς ἐμπλουτισμὸς σὲ νικέλιο παρουσιάζεται ἐνίοτε καὶ σὲ βωξιτικὰ κοιτάσματα π.χ. στὸ κοίτασμα Μάρμαρα Μεγάρων (de Weisse 1967). Γιὰ τὸ δευτερογενῆ ἐμπλουτισμὸ τῶν κατωτέρων τμημάτων τῶν βωξιτικῶν κοιτασμάτων μὲ σίδηρο θὰ ἀκολουθήσει ἄλλη ἐργασία.

Βωξιτικὰ κοιτάσματα, ποὺ γενετικὰ συνδέονται ἄμεσα μὲ ἐκρηξιγενῆ πετρώματα, σπανίζουν στὴν Ἑλλάδα, ἀπαντοῦν σὲ ἐμφανίσεις σχετικὰ μικρὲς καὶ δὲν εἶναι ἐμπορεύσιμα, λόγω τῆς ὑψηλῆς περιεκτικότητας αὐτῶν σὲ SiO_2. Τὸ Al_2O_3 δὲν δείχνει μάλιστα καμμιὰ κανονικὴ ἐξάρτηση ἀπὸ τὴν περιεκτικότητα τῶν βωξιτῶν σὲ Fe_2O_3, ἀλλὰ μεταβάλλεται ἀκανόνιστα, ὅπως στὴν περίπτωση τῶν σιδηρομεταλλευμάτων λατερικοῦ τύπου.

Οἱ ἀποχωρήσεις τῆς θάλασσας, μὲ τὶς ὁποῖες συνδέεται ἡ γένεση τῶν βωξιτῶν, μποροῦν νὰ θεωρηθοῦν σὰν ἀντίκτυπος διαφόρων ὀρογενετικῶν φάσεων, ποὺ ἔδρασαν στὶς ἐσωτερικὲς ζῶνες τοῦ ἑλληνικοῦ χώρου.

Τὸ ἴδιο ἰσχύει καὶ γιὰ τὰ δορυφόρα καὶ ἐμβόλιμα βωξιτικὰ στρώματα, δηλαδὴ τὰ φακοειδῆ βωξιτικὰ σώματα, ποὺ παρεμβάλλονται στὰ κατώτερα καὶ ἀντίστοιχα στὰ ἀνώτερα τμήματα τῶν ἀσβεστολίθων ὀροφῆς τοῦ 2ου βωξιτικοῦ ὁρίζοντα. Ἡ παρουσία τῶν δορυφόρων αὐτῶν στρωμάτων καὶ ἡ ἔλλειψη γωνιώδους ἀσυμφωνίας μεταξὺ ἀσβεστολίθων — δαπέδου καὶ — ὀροφῆς ἐνισχύει τὴν ἄποψη (Κισκύρας 1978) ὅτι πολλὰ βωξιτικὰ κοιτάσματα προέρχονται ἀπὸ τὴν καρστοποίηση ἀνθρακικῶν πετρωμάτων (κατὰ κύριο λόγο ἀσβεστολίθων) ποὺ κατὰ τὴν ἰζηματογένεση μολύνθηκαν ἀπὸ ὀφιολιθικὰ ὑλικά.

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