ORIGIN OF THE TERTIARY RED BEDS IN THE NORTHERN PART OF THE DUERO BASIN (SPAIN),

II. COMPOSITION AND GENESIS *).

BY

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ABSTRACT

In this second paper the red beds outcropping in the northern part of the Duero basin have been treated regarding their mineral and pebble composition, chemical parameters, and surface textures of quartz sand grains, taking as basis the results reported in the first paper.

These deposits originate from soils in the source area, and have been rapidly supplied into the basin by braiding rivers. Heavy mineral associations and pebble composition prove the source area to be lying north and west of the area of deposition. Ferric iron oxides, clay mineral associations, and hydrogen ion concentrations point to a red soil formation in the source area which had not yet attained the laterite stage, but which had already suffered alkaline leaching. The presence of frosted and pitted quartz sand grains and the occurrence of marls are due to the high carbonate content of the waters in the area of deposition, which is caused by dissolution of limestones in the source area.

The general conclusions from the analyses are: (1) that the red beds are "primary detrital" in the sense of Krynine; (2) that the climate in the mountain area during the red soil formation is presumed to have been a tropical savannah climate, that is, warm and fairly humid, at least seasonally; (3) that the climate was drier in the basin, which favoured the preservation of the red beds.

Furthermore, from the presence of blue tourmaline grains within a limited zone, an ancient course of a river in the basin at that particular time could be reconstructed, which gives another indication for a south-easterly drainage direction.

INTRODUCTION

The sedimentological description of the red beds which crop out in the northern part of the Duero basin alongside the foot of the Cantabrian Mountains

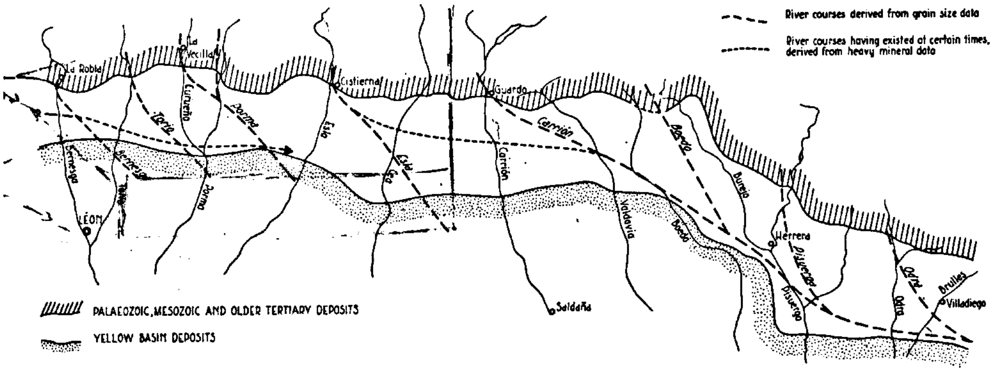

Fig. 1. Schematic map of the presumed courses of the rivers which deposited the red sediments (after data from Mabesoone, 1962).

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is divided into two parts. The first part, published earlier, treated the grain size, pebble roundness, sand grain roundness and sphericity, and contained information on locations, sampling, lithology, and the geological setting of the red foreland deposits. The present, second part treats the mineralogy, pebble composition, chemistry, and surface textures of the quartz sand grains, and gives a discussion of the origin of the sediments.

The data on the areal distribution of the grain sizes and of the facies, contained in the first part, permitted the conclusion of a transport direction towards the SE. This Tertiary river direction is used here for grouping other data, e.g. the heavy mineral associations. A schematic map (fig. 1) shows the approximate directions of these Tertiary rivers.

MINERALOGICAL COMPOSITION

Methods

The samples were treated with the usual method (Edelman & Doeglas 1933) in order to obtain the heavy mineral fraction and the light mineral fraction. both $< 500\ \mu$. During the same treatment the coarse sand fraction (1000—500 μ) was also collected.

The clay fraction ($< 1\ \mu$) used for x-ray analysis and for the determination of the total cation-exchange capacity of the clay, was obtained by a method developed by Favejee already described (Mabesoone 1959, p. 137). The x-ray diagrams, made with the Guinier-De Wolff camera using CuKα-radiation, were filmed by the Crystallographical Section of the Geological Institute of the Leiden University. Cation-exchange capacities (C. E. C.) of the clay fractions were determined by a method in which Ca-acetate was used for saturation, and, after washing with alcohol, Na-acetate for replacement, because it is preferable to use small cations for both (Sawhney & others 1959). The exchanged Ca-ions were determined volumetrically; the C. E. C. values, measured at pH 7, are given in milli-equivalents per 100 grams of clay.

Carbonate minerals were determined chemically. In order to obtain the iron oxides soluble in strong acid some samples were treated without acid. The heavy fraction of these were obtained as previously described. In the slides the minerals of the opaque fraction were determined optically with a stereoscopic polarizing microscope, using the properties given by Milner (1952), Pettijohn (1957), and Arribas Moreno (1960) for distinguishing the various minerals. Further confirmation of the optical determinations was obtained by x-raying some samples; the results show good agreement.

Heavy minerals

In fig. 2 the average heavy mineral composition for each ancient river system is given. It is clear that there are no great differences. Tourmaline, zircon, and rutile form the greater part of the translucent heavy mineral fraction (60—75 %); together they represent the group of "common" minerals. Staurolite, andalusite, kyanite, sillimanite, and topaz are designated as the group of the metamorphic minerals.

In the drainage areas of the Tertiary rivers Bernesga, Torio, and Porma in the W, and in that of the Odra in the E, the content of metamorphic minerals

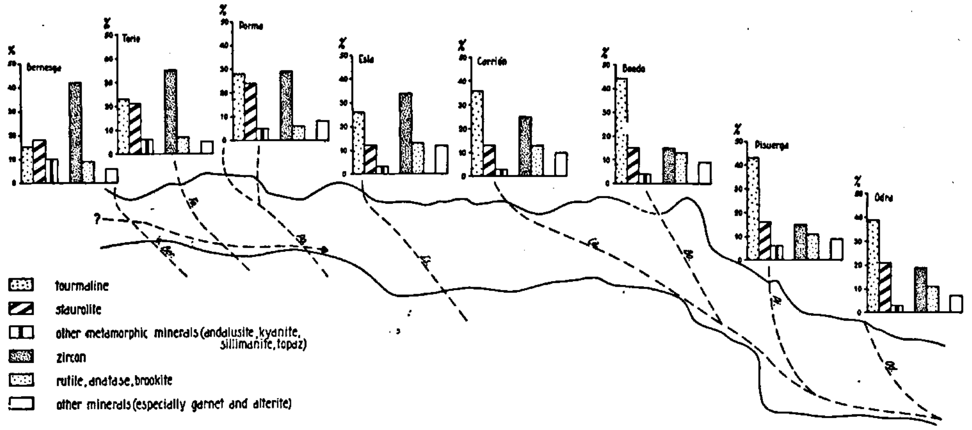

Fig. 2. Geographical distribution of the heavy mineral associations, grouped according to the presumed Tertiary river courses.

is fairly high (24—29 %), higher than in the drainage areas of the other Tertiary rivers (15—22 %). The tourmaline content increases from W to E, whereas the zircon content decreases in the same direction.

Because the heavy mineral composition is a valuable index of provenance, we have added the few data on the sediments of the source area (table 1),

TABLE 1

Some data of heavy mineral composition of weathering products of sediments in the Cantabrian Mountains (after Nossin 1959)

	tourmaline	staurolite	other metamorphic minerals	zircon	rutile/anatase/ brookite	others	observations
Coarse-grained Wealden deposits	46	5	—	27	11	11	—
Fine-grained Wealden deposits	8	—	20	54	6	12	other metamorphic minerals 20 % topaz
Triassic	37	18	—	26	4	15	5 garnet
Curavacas conglomerate	6	—	2	38	27	26	others: 19 alterite, 5 garnet
Devonian	13	—	—	50	10	27	9 garnet
Fine-grained Westphalian deposits	26	12	—	32	14	16	7 garnet

after Nossin (1959). Unfortunately, only some analyses from the E part of the mountain region are available, especially from the Mesozoic deposits. Little is known of the heavy minerals found in the region of the present Carrión river and further to the W. There are as yet no published reports on that area, and only some provisional data could be used.

Much has been written about the resistance of the so-called common minerals. It is known that tourmaline and zircon can also weather. Because these two minerals are abundant in the red beds, they have been studied in some more detail. The results will be discussed below.

It could be demonstrated that the differences in heavy mineral associations are not due to differences in grain size composition. It is true that zircon and rutile are more abundant in the finer sizes than in the coarser ones, while tourmaline shows the reverse (see table 2, showing a heavy mineral analysis of five size classes of a representative sample, a very sandy loam). However, nearly all deposits in the same drainage area, the coarse as well as the fine ones, possess the same average heavy mineral composition. Thus, for instance, the sediments in the ancient Bernesga drainage area all have a high zircon content, and all those in the ancient Pisuerga drainage area a low one, notwithstanding the fact that conglomerates occur in the deposits as well as clayey loams. Hence, the heavy mineral associations cannot be explained by differences in grain size.

TABLE 2

Granulometrical variations of heavy minerals in a very sandy loam

	420—300 μ	300—210 μ	210—150 μ	150—105 μ	105—50 μ
number of grains counted	*25*	*51*	*100*	*100*	*100*
tourmaline	52 %	58 %	64 %	46 %	21 %
zircon	—	—	1	6	39
rutile/anatase/brookite	—	4	13	14	18
garnet	4	—	2	7	1
alterite	32	22	6	7	2
staurolite	4	6	7	12	13
kyanite	—	—	2	4	4
andalusite	—	8	4	1	—
others	8	2	1	3	2

Light minerals

Results of light mineral analyses are not given in a figure. The light fraction of each sediment contains 93—100 % quartz, any remainder consisting of very worn and strongly altered feldspars. Since the deposits in the source area are often rich in quartz and always poor in feldspars, the absence of these latter minerals in the red beds is due to provenance and not to weathering in soils or to disappearance during transport.

Clay minerals

The quantity of each clay mineral present could not be expressed in exact percentages, but is given as five classes of magnitude: dominant, frequent, scarce, rare, and traces. The results are shown in table 3.

TABLE 3

Clay mineral composition of some representative samples

	illite	kaolinite	chlorite	quartz	C.E.C.
Be 1	D	S	—	T	21.77
Be 11	D	F	—	T	17.38
T 13	D	F	T	T	40.07
Po 2	D	F	T	T	25.44
Po 18	D	S	—	T	22.45
E 5	D	F	—	T	16.02
E 19	D	F	—	T	24.58
Ca 6	D	S	R	T	27.05
V 20	D	T	—	T	18.26
V 24	D	T	—	T	22.26
V 26	D	S	—	T	19.87
V 29	D	R	—	T	17.91
V 32A	D	R	—	T	19.40
V 32C	D	T	—	T	21.10
B 6	D	F	—	T	16.10
B 31	D	R	T	T	38.89
P 1	D	F	—	T	22.94
P 30	D	R	T	T	24.75
O 5	D	T	T	T	30.92
O 15	D	R	T	T	20.68

D = dominant, F = frequent, S = scarce, R = rare, T = traces.

It may be observed that the associations are fairly monotonous. Illite is the dominant clay mineral in all samples. Kaolinite occurs in varying quantities; it is never dominating, sometimes frequent, especially in the W part of the area investigated, and in other cases scarce, rare, or only present in traces. In a few samples traces of chlorite could be distinguished. Finally, the quartz content of the clay size fraction is very low, although quartz is present in all samples.

C. E. C. values are added in table 3. They range between 16 and 40, the majority lying between 17 and 30. Since ion-exchange in clays is dependent on the crystal structure of the mineral (Carroll 1959), the values serve merely as a further confirmation of the clay mineral composition of the sediment. C. E.C . values for kaolinite range between 3 and 15, for illite between 10 and 40, for chlorite from 10—± 40, and for quartz $< 2\ \mu$ the value is ± 5. Indeed, the values measured for each sample agree with its clay mineral composition. Because illite predominates, C. E. C. values range between 16 and 40, the average being 23.40. The samples showing the presence of kaolinite generally have exchange capacities lower than the average, whereas those containing traces of chlorite cannot be distinguished from those without that mineral as to their C. E. C. The few deviating values found may be due to a lower crystallinity which often occurs with illites.

Carbonate minerals

Because the preliminary treatment for heavy mineral analysis was performed with strong acids, the soluble carbonates were removed. They were therefore not determined optically. Only a few samples were chemically analyzed for their content of carbonate minerals. It was determined that the carbonates which form the cement of the deposits consist for the greater part of calcite (± 90 % Ca, ± 8 % Mg, and ± 2 % Fe).

Iron and titanium oxides

The opaque fractions of the heavy mineral separates contain 40—50 % goethite, 33—40 % hematite, 14—25 % leucoxene, and 0—2 % magnetite or ilmenite. It is striking that the greater part of the iron oxides, all in a ferric form, consists of goethite. Hematite, although present in a fairly great quantity, never predominates.

The mineral determined optically as leucoxene proved to be rutile according to the x-ray diagrams. This is in good agreement with the data published in Dana's textbook (Palache & others 1944).

Magnetite and ilmenite cannot be distinguished from each other by optical methods, and the percentages found were too small to be determined in the x-ray diagrams.

PEBBLE COMPOSITION

By far the greater part (90—98 %) of the pebbles in the conglomerates are quartzites. The few other components found are: some quartz (2—5 %), a few limestones (1—3 %), and also some pebbles derived from very local deposits in the source area. Generally these latter components were found near the northern boundary of the belt with red beds (Wolf 1959). Because of the uniformity of the pebble associations they are not shown in a figure.

CHEMICAL PARAMETERS

Hydrogen ion concentration (pH)

The pH of all samples was measured electrometrically in an aqueous solution. The results were arranged in three groups, as proposed by Krumbein & Garrels (1952). These authors distinguish an acid environment (pH below 7.0), a neutral environment (pH 7.0—7.8), and an alkaline environment (pH over 7.8).

The sediments containing more than 10 % of carbonate matter all have pH values between 7.8 and 9.0. Those which contain 3.5—10 % $CaCO_3$ have the same values with only a few exceptions. In the deposits with 0.1—3.5 % of carbonate matter, the pH values of the aqueous extracts are scattered over a wide range: 17 samples have pH values of less than 7.0, 10 samples are neutral, and 15 samples have values over 7.8. Lastly, among the sediments without carbonate matter 17 samples have a pH < 7.0, and 9 samples a value > 7.8, no sample having a neutral value.

Although Emery & Rittenberg (1952) found that interstitial water of muds has a slightly higher pH than the waters in which they accumulated, this fact has no significance for the samples treated here because it was found that almost no sample has a pH value just as high as the class boundary. This means that if, for example, an alkaline sample really had a lower pH at the time of its deposition, it certainly did not have neutral value then.

Because calcite precipitates only in an alkaline environment, (pH of at least 7.8) it is understandable that the red beds which contain a high percentage of carbonate matter all belong to the alkaline group. The deviating values in the data will be explained in the discussion.

Ferric/Ferrous ratios

The ferric/ferrous iron ratio of some representative samples with different red colours was determined chemically with the usual methods, following the principles elaborated by Janov (1955). All the ratios determined were 5:1 or higher, which agrees with the results of that author from his study of the origin of red and grey colours in sediments. The intensity of the colour depends on the total amount of iron present in the sample. Furthermore, the red pigment is concentrated in the finer size classes (silt and clay), although many sand grains possess a thin coating of iron oxide pigment; very few grains of ferric iron were found. Accordingly, the deposits show an intense coloration, in which the deep red colours of hematite dominate over the orange ones of goethite. In fact, the calcareous sandstones, which have only a low silt and clay content, are less deeply coloured. The colour of the conglomerates is caused by the high silt and clay content of their matrix, and by the coating of red clayey material around each pebble.

SURFACE TEXTURES OF QUARTZ SAND GRAINS

Besides roundness and sphericity, which have already been discussed in the first paper on these deposits, the surface textures of the sand grains determined during roundness measurements are of importance. The grains have been grouped according to their surface character into four classes: (1) not-worn grains, (2) brilliant grains, (3) frosted grains, and (4) pitted grains. The first three classes were introduced by Cailleux (summary 1956). The fourth group, which was added later by various authors (LIGUS 1958, Chichagov 1959), is also represented here.

Table 4 gives the results of these analyses, grouped according to their geographical position in relation to the presumed courses of the Tertiary rivers. The percentage of brilliant grains increases from W to E. The low percentages of frosted grains show the same increase, and the percentages of pitted grains are low in the Bernesga and Torio drainage areas, but higher in the drainage areas of the other courses.

TABLE 4

Geographical distribution of the different classes of surface textures of quartz sand grains

		brilliant grains	frosted grains	pitted grains
Tertiary	Bernesga	10 %	5 %	11 %
	Torio	12	3	15
	Porma	12	2	24
	Esla	20	7	23
	Carrión	23	7	27
	Boedo	22	5	25
	Pisuerga	24	7	26
	Odra	25	9	30

DISCUSSION

Depositional environment

From data on grain size composition, especially from its distribution over the whole area in which the red beds are found, it could be concluded that the sediments were deposited by braiding rivers on a piedmont alluvial plain. Now that data is available on mineralogical and chemical composition there is no need to change this conclusion, although it must be said that such analyses are not well suited for determining the depositional environment. Only the presence of marls, the pH values, and sometimes the clay mineral composition give some help.

Clay minerals. Because the red beds are deposits of braiding rivers, and possibly sometimes of very weakly alkaline lakes, the clay mineral composition reflects only that of the source area (Grim 1958, Weaver 1958) and has not been changed in the area of deposition.

Marls. In the E part of the investigated area some marly sediments are found. They also have a reddish colour. The analytical results and their geographical distribution are given in fig. 3. All deposits occur in the lower parts of the outcrops, though in the upper parts of the red bed series. There are two kinds: those with 25—31 % carbonate matter (actually sandy marls), and those with > 45 % carbonate matter. Sediments belonging to one of these groups are

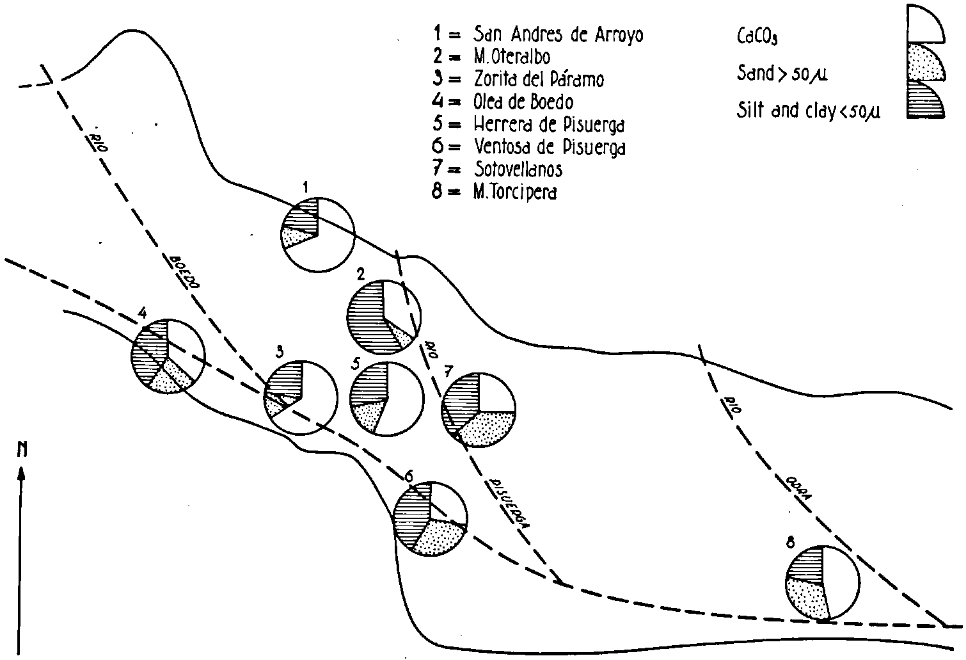

Fig. 3. Geographical distribution and composition of the marls in the eastern part of the investigated area.

not typical for one special region, but more for one special level. The development of these two kinds of marl is then due more to the time at which they were formed. Those marls which contain the higher percentage of carbonate matter are found in the lower levels, those of the other group occur in the upper levels, although these differences are not great (only some 20 metres).

Marls from a continental region are generally deposits of lakes or ponds, in which fine clastic particles were also deposited or flocculated from a saline solution. These particles, in this case, gave their colour to the whole deposit. Sedimentation of the carbonate matter could occur by either loss of CO_2 in a warm climate, or by activity of microorganisms, or by a certain amount of evaporation which caused an over-saturation of carbonate matter in the water. The adjacent Mesozoic limestones could provide a high content of calcareous matter to the water in the basin. The presence of the marls with their fine red clastic components points in this region to a warm and fairly dry climate. The marls still contain a considerable sand content; thus from time to time a supply of rather coarse material occurred, possibly via a river flowing into such a lake or pond, which could develop because the underlying bed was fairly impervious, being often a silty clay or a very clayey loam.

pH. Hydrogen ion concentration gives some information on the waters in which the deposits were laid down and on those which percolated through the already deposited sediment. Only a few investigators have attempted to use acidity-alkalinity values for geological interpretations.

Stevens & Carron (1948) introduced the abrasion-pH values obtained by a grinding technique. They established a scale by which different minerals may be distinguished. An abrasion-pH of a whole sample thus gives an average of the minerals present. Because the samples of the red deposits in the Duero basin consist of quartz grains, carbonates, some iron oxides, heavy minerals, and clay minerals, their abrasion-pH, after data given by Stevens and Carron, should vary between 6 and 8. It is fairly difficult to distinguish different environments within such a narrow range, so that this approach to the problem was not followed.

The most extensive data on the geological significance of pH values from determinations in aqueous extracts was provided by Atkins (1930), who determined hydrogen ion concentrations of several natural waters and found for non-calcareous river and lake waters pH values of between 6.5 and 7.0, and for calcareous river and lake waters values between 8.0 and 8.4. Because of the significance of calcareous matter and iron hydroxides in sediments, he discussed the environments in which these minerals dissolve and precipitate. His results, or at least those of interest to this study, are given in table 5.

A point of importance is the difference in precipitation of ferrous and ferric salts as hydroxides. Because in the red beds iron is present in a ferric state, and the pH values for these red beds are all higher than 5.0, even those of the deposits which do not contain carbonate matter, the iron in these sediments could not have been supplied in solution by river water. Hence, it must have been transported in precipitated form, either as coatings around quartz grains and other minerals or as grains consisting only of iron oxide. It also points to an absence of organic matter which favors the solution of iron salts.

Secondly, calcium carbonates precipitate at pH values > 7.8 (Krumbein & Garrels 1952). Because calcareous river waters, such as must have come from the Cantabrian Mountains with their extensive limestone deposits, have pH

TABLE 5

pH values of some natural waters, and some pH values at which precipitate some hydroxides (after Atkins 1930)

natural waters:		
rain in open country	pH 5.9	
non-calcareous river and lake water	6.5—7.0	
calcareous river and lake water	8.0—8.4	
springs in calcareous regions	6.0—6.6,	varying with relative proportions of calcium bicarbonate and free CO_2

pH of distilled water in a good quality resistance glass tube 7.05—7.10

approximate pH values for precipitation of hydroxides or basic hydroxides:

	initial precipitation begins at	heavy precipitation at
ferric	pH 3.0	pH 5.0
ferrous	5.1	7.0
magnesium	10.0	10.5
calcium	11.0	12.0

Carbonates are less soluble than hydroxides, but bicarbonates of calcium and magnesium become increasingly soluble above pH 9; in more alkaline solutions only carbonates exist, and, owing to the removal of CO_2 during photosynthesis, may be precipitated in quantity in the presence of abundant plant life.

values of about 8.2, the calcareous matter was transported as bicarbonate and carbonate in the presence of carbonic acid. When entering the area of deposition, where the climate was certainly warmer than in the mountains, the waters lost part of their CO_2 content, resulting in a precipitation of these carbonates. Loss of carbonic acid by photosynthesis could also have occurred, because there must have been fairly abundant plant life. This we conclude from the high clay content of the red deposits, which clay could have been sedimented by sieving-out by these plants.

The sediments which have pH values lower than 7.8 but still have a certain carbonate matter content (0.1—3.5 %), were analyzed to determine the nature of this carbonate. In such sediments it proved to consist not of a cement of calcite but of a number of limestone fragments of small size (fine sand and coarse silt). This type of deposit has only been found in the drainage areas of the Tertiary Bernesga and Esla rivers, and especially in those regions where the sediments were not mixed with those supplied by other streams, and then only over a small vertical range. Because of the small size of the limestone fragments their source rock could not be determined. It should be noted that the deposits without carbonate matter and having an acid pH value (< 7.0) were found in the same drainage areas, and, among those of the other Tertiary rivers, only in that of the Torio, but then near the mixing zone with the ancient Bernesga. The explanation for this distribution may be that during that particular period of the sedimentation these rivers did not erode limestones, or that they flowed through totally decalcified soils on limestones or other sediments.

Transportation

What has been said with regard to the depositional environment can also be applied here: mineralogy and geochemistry are not suited to providing data on transportation either, with the possible exception of the clay minerals. The transportation was so rapid that these could not alter on the way.

Provenance and circumstances in the source area

Because provenance and certain circumstances in the source area are closely related, we will here discuss them together in terms of the data obtained by the various analyses indicative for both.

Heavy mineral associations. From table 1 it may be concluded that the Paleozoic sediments in the source area provided chiefly zircon, rutile, and tourmaline, being "common" minerals. Metamorphic minerals, especially staurolite, came from the Triassic deposits. The Wealden sediments contributed much tourmaline. Therefore the increasing percentage of tourmaline and staurolite in the drainage areas of the ancient Boedo, Pisuerga, and Odra rivers is due to a supply from the region with Mesozoic sediments, where extensive outcrops of Triassic and Wealden deposits can be found (Ciry 1939). High percentages of zircon are found in the Carrión area and further to the W; this can thus easily be explained by the supply from the Paleozoic sediments in the Cantabrian Mountains. Because a narrow strip of Mesozoic sediments still occurs S of the whole of the Paleozoic belt, their heavy mineral content also had some influence on the associations in the red bed region. But here no sediments of Triassic age have been found, so that the high staurolite content, especially in the Porma region, remains unexplained. Although it is possible that the Triassic belt could have extended somewhat farther to the W, this distance seems to be too great (more than 70 km).

When considering the analyses of the separate samples in these W regions, two associations can be distinguished. A number of samples show a high zircon and rutile content, others a high staurolite and tourmaline content. As can be

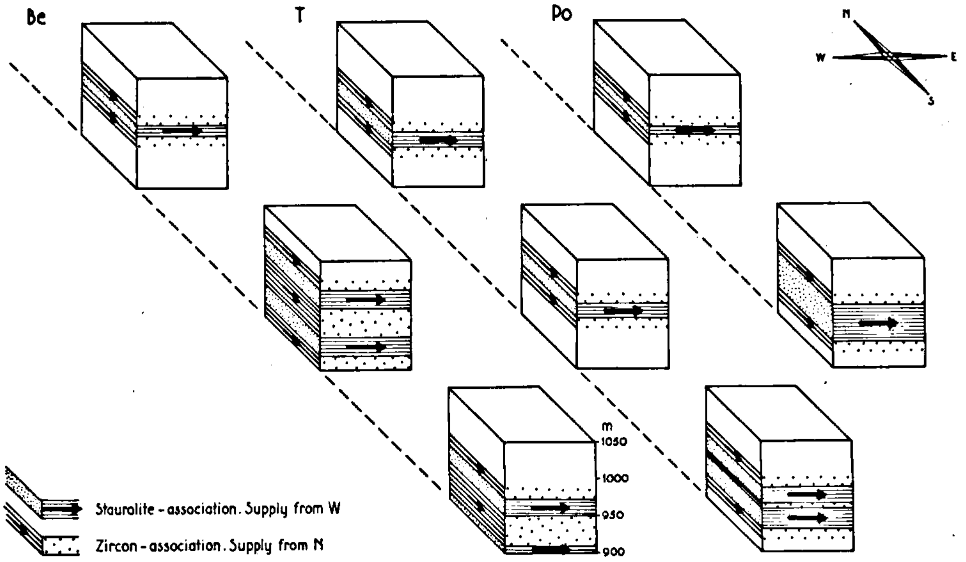

Fig. 4. Supply directions derived from heavy mineral data in the region west of the river Esla.

seen from table 1, the Paleozoic deposits provided almost exclusively "common" minerals; thus the red layers which show an association with a high percentage of zircon and rutile must have been supplied by the Paleozoic mountains lying N of them. This means that the red sediments which have a high staurolite and tourmaline content, could have come from another direction. In this case it must be remembered that the Tertiary basin has its border 8—10 km in a westerly direction from La Robla and the Bernesga valley (Mabesoone 1962, fig. 2). There the Galician-Leonese mountains are situated. Some rivers which at present drain that area flow towards the basin, others towards the W, but there are indications that the rivers which at present flow towards the Atlantic Ocean in the W (e. g. the river Sil; Sluiter, oral communication), in Tertiary times also flowed towards the Duero basin. Thus staurolite may have come from Galicia, a high-grade metamorphic region (fig. 4). The staurolites in the red beds would then have been derived from Paleozoic deposits sedimented at the foot of the Galician region (Boschma, personal communication), and possibly partly from the Galician block itself.

Tourmaline. This mineral derived from Paleozoic as well as from Mesozoic sediments in the Cantabrian Mountains. The most frequent types are the brown, green, and yellow varieties; a few pink grains were also found. All these grains show the typical pleochroism. They are angular to subangular. Because the sediments in the mountain area are weakly metamorphic, tourmaline could have been formed or deformed in them. The low roundness of the grains suggests that they do not derive from not-altered sediments (Krynine 1946), that is to say they do not indicate a second cycle.

In a number of red layers a fairly large amount of blue tourmaline (variety indicolite) was determined. These grains, with only a few exceptions, show no pleochroism, and thus represent basal, or nearly basal sections. In fig. 5 their geographical distribution among the analyzed layers is given. From this it may be concluded that at a certain time a rock was exposed in the mountain area from which a great quantity of blue tourmaline weathered out. Some blue tourmaline is also found at present in this region (Oele, oral communication). These grains were taken up by the Tertiary Esla and transported downstream. The whole course of the Esla at that particular time thus can be followed, and even its equilibrium profile can be constructed. All this confirms the opinion expressed earlier that the river flowed from the mountain area in a south-easterly direction on a rather flat surface. At the site where it joined with the ancient Carrión river the slope increased, to become smaller again some kilometres downstream (fig. 5).

Staurolite. The presence of this mineral in the Tertiary deposits is rather interesting. Although it is considered to be a stable mineral, it does not reach the stability values of minerals such as rutile, zircon, and tourmaline. The grains found in the red beds, especially those in the W part of the investigated area, range over a great number of size classes and also over a great number of roundness classes, although angular and subangular grains are more frequent than the rounded forms. Many grains show carbonaceous inclusions, so as to become nearly alterites. In these cases pleochroism can no longer be seen, and the grain must be recognized by its moderate birefringence. Generally the grains show very few signs of solution and corrosion. As we have already said, they must have derived from the metamorphic rocks of the Galician area,

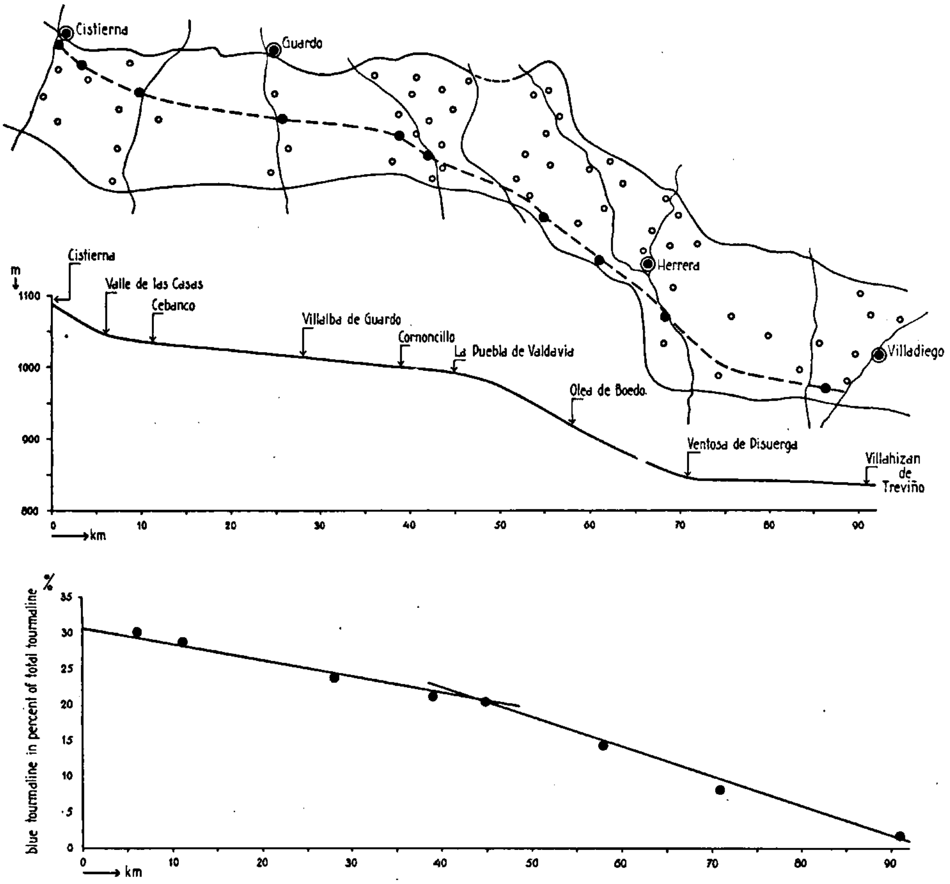

Fig. 5. Ancient Esla course as concluded from the occurrence of blue tourmaline grains.
Upper: black dots: localities where blue tourmaline was only found; open circles: localities where no blue tourmaline was found.
Middle: longitudinal profile of the conjectured ancient Esla course.
Lower: amounts of blue tourmaline along the conjectured ancient Esla course.

then deposited in the Lower-Paleozoic sediments at the E boundary of that area, and afterwards supplied by the latter to the Tertiary red beds. Evidently they did not undergo any solution during that long period.

Zircon. Poldervaart (1955) rightly states that the study of size and shape of zircon grains is not very useful in paleogeographical investigations because of the minor changes over even large distances. But although zircon is a very resistant mineral some varieties of it, especially the hyacinth and malacon types, are susceptible to weathering (Carroll 1953). She observed that zircons in lateritic soils are often strongly corroded, and she ascribed this to attack by alkaline solutions.

In the heavy mineral slides of the red beds, 5—10 % of the zircon grains are of the hyacinth type, while malacons are absent. The so-called "normal" zircon type grains are subangular, subrounded, and rounded, and they do not show any sign of weathering. The zircon grains of the hyacinth type, however, do actually show some attack, but only to a small extent. This may lead to the conclusion that the pink-coloured zircons did not suffer a strong alkaline leaching in a lateritic soil profile. The weakly alkaline solutions passing through the soils in the source area, and possibly also later in the basin sediments, nevertheless could attack the hyacinth zircons to a small degree.

Opaque minerals. Miller & Folk (1955) argued that, because all red beds contain detrital magnetite or ilmenite, the formation of these deposits depends primarily on the presence of igneous or metamorphic source rocks, and is only indirectly dependent on climate or depositional environment. The data provided by the mineralogical analyses of the investigated red beds points to just the reverse. Firstly, magnetite and ilmenite are present only in a very small quantity. Secondly, in the source area almost no igneous or metamorphic rocks are found. Further, the red pigment is concentrated in the finest size grades, although thin coatings around sand grains are also present. It follows that the relations found by Miller and Folk do not hold for the red beds in the Duero basin, and that the objections to their theory made by Dunbar & Rodgers (1957, p. 211) proved in this case to be valid.

Clay mineral composition. As has been stated before, the clay mineral associations found in the investigated red deposits reflect their composition in the source area, in this case the red soils which must have covered the Cantabrian Mountains.

The circumstances in which the clay minerals generally form are mentioned by Carroll (1959, table 2). Kaolinite develops in soils under intense leaching and oxidizing or reducing conditions, at pH values of about 4. Illite or hydrous mica may form in a fairly wide range of conditions, as a transition type, but not under intense leaching, at a wider range of pH values; it may form first in soils near freshly weathered parent material. Chlorite develops in all types of rocks, but generally not in soils, under a wide range of conditions, probably at a pH ± 7, but it remains more stable in an alkaline environment; in the Cantabrian Mountains it could have been formed from micas which are present in that area e. g. in the Oville sandstones (Oele, oral communication).

Illite is the dominant clay mineral, and because it forms under a wide range of conditions no definite conclusions can be drawn on the basis of the presence of this mineral alone. Illite dominates in almost every deposit, and can be considered to have the same significance in fine-grained sediments as does the quartz in the coarser-grained ones (Weaver 1958).

Kaolinite, which is present in the samples in a smaller quantity, can give more information. It certainly formed in the source area under specific conditions, with alkaline leaching. Because initial weathering leads to formation of illite and montmorillonite, advanced weathering, in more thoroughly leached parts, often results in the formation of kaolinite (Hooks & Ingram 1955).

From all this it may be concluded that the soils developed in the source area were not mature, and were not true laterites but possibly tropical red soils. Furthermore, because the rocks in the source area are poor in feldspars the formation of kaolinite was not favoured (Krebs & Tedrow 1958). Then, the associations of clay minerals found in the red basin deposits are due to (1) a mixing of different soil types or horizons, and (2) to associations already present in the shales from which they derived without further alterations.

Pebble composition. Because 90—98 % of the pebbles in the conglomeratic beds are quartzites, this may point either to a textural maturity of the red deposit or to a supply of great amounts of these pebbles from the source area. When treating the pebble roundness in the first part of this paper (Mabesoone 1962), the fact was mentioned that in the mountain area extensive Carboniferous pebbly deposits occur which consist of quartzitic pebbles. These are the well-known Curavacas conglomerates of Westphalian age, and moreover some conglomerates occurring at the borders of the Stephanian coal basins (De Sitter 1961). Some quartzitic rocks also occur in the mountain area which could have directly provided pebbles to the Tertiary red beds. In the W a great supply from Silurian quartzites took place (Bataller & Sampelayo 1944). It can thus be said that the quartzites have only a small significance for determination of provenance and circumstances in the source area, and for textural maturity. The same can be said of the few quartz pebbles found.

The limestone pebbles all came from Devonian and older limestones, and, as we have mentioned earlier (Mabesoone 1959), no pebble from the Carboniferous "caliza de montaña", at present so well exposed, has been found.

In the Valdavia region and further to the E some pebbles of Triassic sandstones are met with. For the eastern river systems this is quite understandable, because E of the Pisuerga valley in the Cantabrian Mountains extensive Triassic sediments are exposed. But the finding of a small number of such pebbles (in quantities $< 1\,\%$) in the present Valdavia valley, especially in the lower conglomeratic layers of the outcrop near Vega de Riacos described earlier, and more to the N in the valleys of the small affluents of the river Valdavia, would lead to the conclusion that the Triassic sediments extended farther to the W than at present. In the conglomerates now found in the present Carrión valley, Triassic pebbles are absent, as they are in a more westerly direction. Hence, Triassic deposits could have reached up to nearly the Carrión valley. So the Mesozoic deposits, which in Eocene and Oligocene times occupied a fairly large area in the Cantabrian Mountains (Mabesoone 1959), were at the time of the red bed sedimentation not yet reduced to their present occurrence. At the S border of the mountain range these Mesozoic sediments are confined to those of Cretaceous age. Therefore, Triassic deposits must have been present somewhat inside the mountains. The last remnants must have been removed about the time of the red beds.

Quartz sand grain types. Although Cailleux (1956) states that brilliant rounded grains obtained their shape and surface textures during river transport, Kuenen (summary 1959) found in his experiments that this takes an enormous length of time, and hence occurs only during various sedimentary cycles. The lustre of the sand grains seems more likely to be due to a secondary growth under water. But silica precipitates extremely slowly (Krauskopf 1959), and thus during short river transport the grains cannot grow in such a way as to become brilliant. Thus these types must have come from the source area, where such grains indeed are found, especially in the matrix of the conglomeratic layers.

Carbonate leaching may have caused some incipient frosting of quartz grains. Because pitted grains, which may point to a further attack, are frequently found in the basin sediments, the frosting could have taken place in the source area.

Occurrence of rock fragments. In the red basin deposits almost no rock fragments were found, only quartz grains, ferric iron oxides, clay minerals etc. This points to a high state of chemical weathering in the source area, which must be due to an advanced state of soil formation. Thus the parent material of the red basin sediments were certainly soils, and not red bedrock which actually does occur, though much less than non-red rocks.

pH. Hydrogen ion concentration of the leaching water has already been discussed in the paragraph on depositional environment. Ferric oxides must have been formed in the source area. Red weathering includes a leaching in an environment poor in humus, with water which became alkaline from cations of alkalis and alkaline earths from the soil. Because this type of weathering leads first to solution of these alkalis, calcium, and magnesium, and then in a later stage to solution of silica, the neutral to alkaline waters did precipitate the ferric iron. Where these waters drained soils on limestones, they must also have contained a considerable amount of carbonate matter.

Lithification and diagenesis

The character of the sediment makes it unable for the preparation of thin sections. Hence, diagenetic features could be observed only with difficulty.

Cementation of the red sediments could have occurred rapidly just after their deposition. The waters passing through the red bed zone was alkaline and contained dissolved carbonates and bicarbonates. During dry seasons, or at dry places, carbonate matter could precipitate in the pores of the already deposited sediment, so that it became cemented. This cement developed in larger quantities in the coarser than in the finer deposits. At some places even fairly large calcite crystals could grow, as found especially in an outcrop in the present Cea valley (Wolf 1959), and in another in the present Porma valley.

TABLE 6

Percentages of pitted and frosted grains in relation to carbonate matter content

		samples with $< 10\,\%$ $CaCO_3$		samples with $> 10\,\%$ $CaCO_3$	
		pitted	frosted	pitted	frosted
Tertiary	Bernesga	10 %	5 %	15 %	5 %
	Torio	14	3	17	3
	Porma	19	2	25	2
	Esla	20	6	26	8
	Carrión	20	7	30	7
	Boedo	24	4	28	6
	Pisuerga	22	5	28	8
	Odra	22	5	30	9

Frosting and pitting of the quartz sand grains may have occurred both post-depositionally, and already in the source area. Table 6 gives the percentages of pitted and frosted grains in relation to the $CaCO_3$ content of the samples for each Tertiary river system. A general increase towards the E of the percentage of pitted grains in the sediments containing more than 10 % $CaCO_3$ is conspicuous; in the percentages of frosted grains practically no changes are found. There must therefore be a relation between carbonate content and frosting of quartz sand grains. The pitted grains generally still show some traces of previous frosting. Walker (1957) found that frosting of quartz grains is also caused by carbonate replacement along grain boundaries. Such frosting may easily lead to pitting by continuing action (compare Pettijohn 1957). The frosting of the quartz sand grains must thus be due to incipient chemical attack in soils and not to a previous desert climate which may also cause such frosting. Once deposited in the red beds in the basin, the attack by carbonate matter continued to a stronger degree, the more so because the carbonate matter content was higher. This may have caused pitting.

CONCLUSIONS

Origin of the red beds

From comparison of our deposits with the current descriptions of red beds in textbooks (Dunbar & Rodgers 1957, Ruchin 1958), it may be concluded that those found in the northern part of the Duero basin are not of a common type. Firstly, all deposits have a red colour; alternation with green or differently coloured layers has nowhere been found. Secondly, rudites are said to be generally rare in red beds, siltstones and shales being more frequent, but this is reversed in the deposits of the Duero basin. Thirdly, cross-bedding in the arenites has not been found, although channel filling is often present.

However, other characteristics found in red beds elsewhere are present here too. We may mention: poor sorting, absence of fossils, no humus, good roundness of the pebbles, and red colour due to disseminated ferric iron oxides in the finer sized grades.

Generally the use of the term "red beds" implies abundance of hematite. The analysis of the iron oxides showed that here goethite predominates, not hematite. But possibly the deep red colour of hematite nevertheless dominates over the more orange hues of goethite, so that the colour of the deposits as a whole remains deep red.

In the sense of Krynine (1949), the red sediments in the investigated area are "primary detrital". This means that the red pigment developed through weathering in the source area, and was incorporated directly into the sediment derived from these soils after erosion and transport. This implies a special geomorphological and climatic condition in that source area. The region must have been well drained, which points to a certain degree of humidity. The slopes must have been sufficient to maintain the soils above the water table, that is, in the oxidation zone. After Krynine, the climate must have been as follows: for red weathering of silicates a mean annual temperature above 16° C, and an annual rainfall of over 1000 mm, and for red weathering of carbonates the same temperature and a rainfall of over 625 mm. The climate must thus always have been warm; so red deposits are indicative for such a climate (Schwarzbach 1961). The rainfall, however, could have been seasonal.

That the red beds at the foot of the mountains are really primary detrital may be concluded from the following facts: (1) They were rapidly transported by rivers, so that they could not oxidize during transport. (2) The red colour must have been present in the source rocks, because the transporting alkaline waters can only carry ferric iron in a precipitated form as either coatings around grains or as ferruginous concretions. (3) If the red colour had developed after deposition, the sediments would not all have turned red. (4) The sediments in the source area never contained so many red beds that the large amount in the basin could have been derived exclusively from older red beds.

The red basin deposits are connected with fairly deep erosion and rather steep longitudinal river profiles in the mountain area, which provide transport for pebbles and larger gravel components. This points to an early phase of uplift after a period of quiet, in which thick red soils could develop. Van Houten (1948), in his extensive study on the red sediment formation, also comes to the conclusion that most red beds have derived from red soils in their source area.

In the first part of this paper, and in the preceding paragraphs of this second part we pointed to certain circumstances in the source area at the time of sedimentation of the red beds in the basin which may be briefly summed up here: (1) fairly strong vertical erosion; (2) red weathering with an incipient leaching; (3) alkalinity of the leaching water, partly caused by dissolving limestones; (4) fairly high humidity, as shown by the transport capacity of the rivers; (5) a warm climate.

Because the red beds at the northern border of the Duero basin are primary detrital in the sense of Krynine (1949), and must therefore have derived from red soils in the source area, we may draw certain conclusions about the circumstances in the Cantabrian Mountains. During a period of tectonic quiet a red soil formation occurred on all types of sediments in the mountain area. The climate there was warm and at least seasonally humid, possibly a tropical savannah climate. The red weathering led to tropical red soils, and possibly in the higher parts of the mountains to red podsols. Nevertheless, the mountains did not have great altitude because no indications of the existence of former non-red mountain soils could be detected. No laterization took place, because no hydroxides and oxides of aluminum were found, whose formation is a precondition for this process (Mohr & van Baren 1954). Before an advanced stage of soil development, resulting in laterites, was attained, epeirogenic uplift began, and the red soils became eroded and transported. The upper horizons may already have been somewhat further developed, and can have provided kaolinite to the basin sediments. The lower horizons provided the illites. This points to rapid erosion, because after removal of the upper horizons no new upper horizons of the same type could develop because of lack of time. Thus deep erosion took place, cutting V-shaped valleys which gradually undercut the slopes of the interfluves covered with thick red soils. The rivers flowed rapidly and had a fairly steep gradient, so they could carry off large pebbles from eroded conglomerates as well as red mud. This could have occurred seasonally, because a year-round humidity would have led to even laterization. The climate may then have been a tropical savannah climate.

Preservation of the red beds

The area of deposition need not have had the same climate as the source area to preserve the red colour. A number of investigators presume that a drier climate, e. g. arid conditions in deserts, is more suitable for the preservation of red beds (Dunham 1953), because of the many red sediments found associated with evaporites.

Actually, the red beds in the northern part of the Duero basin are not associated with evaporites. If evaporation was much greater than water supply, certainly gypsum would have precipitated because some subterranean waters in the present red bed region and in the adjacent mountain area show a fairly high content of SO_4-ions (ranging between 0.1955 and 0.0102 g/L, see sheet 133 of the geological map of Spain; Almela & Badillo 1956).

Nevertheless, the area of deposition will have been drier than the mountain area, e. g. a savannah climate of the dry type. If the basin had a more humid climate a more intense vegetation would have grown up, resulting in laterization of the soil, confinement of the rivers into narrower streambeds, and more intense weathering in general. Actually, no new kaolinite was formed, the amount of iron and aluminum oxides remained small. So the climate in the basin must have been fairly dry, possibly of the same type as at present (BSa in the sense of Köppen). At present, soil formation on the red beds also results in preservation of the red colour. This means that during the greater part of the Tertiary the climate did not vary very much: it only became gradually cooler and more arid. Although we once stated (Mabesoone 1959) that after the deposition of the older limestone conglomerates in a warm and fairly dry climate this became more humid during the sedimentation of the red beds, we now believe this not to be true. The younger yellow and red clayey layers were deposited in a more arid environment as indicated by the presence of extensive marls and gypsum layers in the basin centre, so the climate in the red bed sedimentation period had an intermediate position. Thus, in general, the aridity of the Duero basin must have increased during the deposition of the Tertiary basin sediments. Sluiter (oral communication) also found similar indications in the W part of the Duero basin. Probably during that whole period the basin was surrounded, with a possible exception in the far SE, by mountain chains which collected the greater part of the precipitation, leaving a dry region in their midst

The only objection to this conclusion would be the occurrence of the thin lignite layer found in the present drainage area of the Carrión river. No pollen has been found in it because of the oxidizing environment. It seems rather possible that the organic material derived from an upstream region during a time of catastrophic high waters. These plant remnants were deposited in a quiet place in the basin and were buried rapidly so as to become lignite.

SUMMARY

In this paper the red beds in the northern part of the Duero basin have been treated regarding their mineralogical composition, pebble composition, chemical parameters, and surface textures of quartz sand grains. The data obtained from these analyses, combined with those from the first paper published on this subject (Mabesoone 1962), give the following results.

1. Differences in the heavy mineral associations reflect supply from different source areas. The association provided by the Mesozoic sediments in the E differs somewhat from that provided by the Paleozoic deposits in the W and centre. Moreover, in the W metamorphic minerals were derived directly or indirectly from the Galician block.

2. Clay mineral associations are presumed to reflect the associations occurring at that time in soils of the source area, because the short transport and the climate in the basin were not favourable for their alteration. Illite points to an initial weathering; kaolinite derived from upper horizons of the presumed red soils.

3. Iron minerals show predominantly ferric forms which developed in the source area, and which were transported in a precipitated form into the basin, giving the red colour to the deposits.

4. The predominance of quartzitic components in the pebbly beds points to a strong erosion of the quartzitic conglomerates and of some quartzites in the mountain area.

5. Hydrogen ion concentration indicates an alkaline environment, caused by solution of limestones and alkaline leaching of soils.

6. The rather great abundance of pitted quartz grains may be due to attack in an environment containing carbonate matter.

7. Deposition took place via braiding rivers, and possibly sometimes in shallow lakes or ponds.

8. The source area must have been covered by a thick red soil which was eroded and carried off rapidly. The red soils, although they were not laterites, indicate a warm climate with, at least seasonally, high precipitation.

9. The preservation of the red beds in the basin gives evidence of a somewhat drier climate in that area.

10. The red beds are primary detrital in the sense of Krynine (1949).

RESUMEN

Las capas rojas ("red beds") que afloran en la parte norte de la cuenca del Duero, han sido objeto, en este trabajo, de investigaciones sobre su composición mineralógica, la naturaleza de sus cantos, los parametros químicos, y los tipos de sus granos de cuarzo. Los resultados de los análisis, juntos con los publicados en el artículo primero sobre este tema (Mabesoone 1962) permiten las conclusiones siguientes:

1. Las variaciones de las asociaciones de minerales pesados reflejan una procedencia de distintos lugares de origen. La asociación procedente de los sedimentos mesozoicos de la parte oriental de la cordillera es distinta de la asociación procedente de los depósitos paleozoicos de las partes central y occidental. Además, en la parte occidental de la cuenca, minerales metamórficos provienen directa o indirectamente del macizo galaico.

2. Las asociaciones de minerales de arcilla presumiblemente reflejan las que se hallaban en aquella época en los suelos de la región montañosa de origen, por no ser propicios el transporte corto y el clima de la cuenca a la alteración de dichos minerales. La ilita indica una alteración incipiente; la caolinita provenía de los horizontes altos de los presuntos suelos rojos.

3. Los minerales de hierro son en su mayoría óxidos férricos que se formaron en la región montañosa, y que se transportaron a la cuenca bajo la forma de precipitaciones, produciendo el color rojo de los depósitos.

4. La predominancia de cantos de cuarcita en los estratos guijarrosos indica una fuerte erosión de los conglomerados cuarcíticos y de las rocas cuarcíticas de la cordillera.

5. La concentración de iones de hidrógeno (pH) señala un medio alcalino, producido por la solución de calizas y la lixiviación alcalina de los suelos.

6. Una abundancia bastante considerable de granos cariados de cuarzo se debe probablemente a un ataque químico en un medio que contiene carbonatos.

7. Sedimentación ocurrió a través de ríos anastomosados, y posiblemente a veces en lagunas.

8. La región fuente debe de haber tenido una cobertura de suelos rojos espesos que se erosionaron y llevaron rápidamente. Los suelos rojos, aunque no lateritas, señalan un clima cálido con alta precipitación, a lo menos estacionalmente.

9. La preservación de las capas rojas en la cuenca indica que había un clima algo más seco en aquella región.

10. Las capas rojas son del tipo "primario detrítico" en el sentido de Krynine (1949).

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