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The late Ordovician carbonate sedimentation as a major triggering factor of the Hirnantian glaciation

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Key words. – Carbonates, Glaciation, CO_2 sink, Hirnantian, North Gondwana.

Abstract. – A new approach explaining the main forcing factor of Hirnantian glaciation is proposed herein. It follows the models associating occurrences of continental glaciations with periods of low atmospheric CO_2 levels. The accumulation of great volumes of carbonates during pre-Hirnantian late Ordovician, in regions where these deposits were previously absent, is suggested as a major sink of atmospheric CO_2. This would have caused an important lowering of the average temperature in the early Hirnantian, after CO_2 values had attained a certain threshold. This process was maintained by other positive feedbacks, such as the short-term carbonate weathering CO_2 sink. An increase of the direct flux of CO_2 from the atmosphere to the oceans by means of dissolution would have been driven by the enhancement of carbonate deposition. The great inundation of the low latitude Laurentia craton during Cincinnatian times and the establishment of a temperate-water carbonate sedimentation on the North Gondwana margin during pre-Hirnantian Ashgill allowed the burying of more than 840×10^{15} kg (1.9×10^{19} mol) of dissolved CO_2. This mass is equivalent to nearly 350 times the present values of atmospheric CO_2. This is important enough to have greatly altered the equilibrium between the CO_2 dissolved in the oceans and the partial pressure of CO_2 in the air, eventually causing an important reduction of the latter. The new model also offers a simple explanation for the end of the glaciation after a short time-span. Glacioeustatic lowering of the sea level, concomitant with the glaciation, would have stopped the extra-sedimentation of carbonate due to the retreat of the oceans from the platforms, closing this CO_2 sink. Pre-glacial CO_2 levels would then recover, due to volcanic and metamorphic CO_2 outgassing. After subsequent melting of the ice cap, oceanic circulation did not recover pre-Hirnantian Ashgill strength, resulting in a strong stratification of ocean waters and precluding the recovery of an extensive carbonate deposition. The well-known positive shift in the $\delta^{13}C$ at the base of the Hirnantian is assumed to have been caused by weathering and dissolution of carbonates, relatively enriched in ^{13}C, during the glacioeustatic regression and exposure of the platforms.

La sédimentation carbonatée ordovicienne : un des principaux facteurs déclencheur de la glaciation hirnantienne

Mots clés. – Carbonates, Glaciation, Puits de CO_2, Hirnantien, Gondwana septentrional.

Résumé. – Une nouvelle approche concernant le déroulement de la glaciation hirnantienne est proposée dans ce travail. Elle s'intéresse aux principaux facteurs clés de cette dernière et associe les effets d'une glaciation continentale à une période de bas niveau du CO_2 atmosphérique. L'accumulation d'un important volume de carbonates au cours de l'Ordovicien terminal pré-Hirnantien dans des régions où ces derniers étaient antérieurement absents est considérée comme un important puits de CO_2 atmosphérique. Cette accumulation pourrait être la cause d'une baisse importante de la température moyenne au début de l'Hirnantien à laquelle s'ajoute un autre processus de rétroaction tel que la météorisation des carbonates. Une augmentation du flux de CO_2 de l'atmosphère vers les océans par dissolution devrait avoir été favorisée par la précipitation de carbonates. L'importante inondation du continent Laurentia, situé à basse latitude au cours du Cincinnatien, et l'implantation d'une sédimentation carbonatée tempérée sur la marge nord-gondwanienne au cours de l'Ashgill (pre-Hirnantien), ont favorisé l'enfouissement de plus de 840×10^{15} kg ($1,9 \times 10^{19}$ mol) de CO_2 dissous. Cette masse représente environ 350 fois la valeur actuelle du CO_2 atmosphérique. Cette précipitation devrait avoir altéré fortement l'équilibre entre le CO_2 dissous dans les océans et la pression partielle de CO_2 dans l'air, entraînant éventuellement une réduction de cette dernière. L'approche développée dans ce travail offre une explication simple pour la fin accélérée de la glaciation. La baisse du niveau marin relatif, attribuée au glacio-eustatisme associée au recul de la ligne de rivage des océans sur les plates-formes, devrait avoir provoqué l'arrêt de la production de sédiments carbonatés et de l'absorption de CO_2. Le niveau de CO_2 préglaciaire devrait dès lors se rétablir à la faveur du dégazage de CO_2 par volcanisme. Toutefois, après la fonte des glaces, les circulations océaniques ne reprennent pas et l'absence des courants instaurés lors de l'Ashgill (pré-Hirnantien) par une importante stratification des eaux océaniques empêche la reprise d'une importante sédimentation carbonatée. Les pics positifs bien connus du $\delta^{13}C$ à la base de l'Hirnantien sont attribués au lessivage et à la dissolution des carbonates enrichis en ^{13}C lors de l'importante émersion des plate-formes.

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INTRODUCTION

Hirnantian glaciation has aroused a keen interest during the last decade due to its apparent anomalous occurrence during times of very high levels of the greenhouse gas CO_2. These levels, according to computer models of the long-term carbon cycle [Berner, 1990, 1992 ; Berner and Kothavala, 2001] and geochemical studies of paleosols [Yapp and Poths, 1992], would have reached 14-18 times (14-18x) the present atmospheric value. This estimate makes it difficult to understand the onset of the Hirnantian glaciation, since the former values represent an apparent anomaly for the models associating occurrences of continental glaciations with periods of low CO_2 levels, such as those recognized during Carboniferous-Permian and late Cenozoic times [Berner, 1992]. To reconcile the postulated CO_2 levels and the well-characterized, short-lived Hirnantian glaciation, Crowley and Baum [1991, 1995] used different energy balances and general circulation models. They estimated that both of them would have been compatible with extreme values of the following parameters : a Gondwana margin adjacent to the South Pole, reduced patterns of solar luminosity, an orbital configuration of minimum summer insolation receipt, and slightly elevated topography on high latitudes. The abrupt changes in oxygen and carbon isotopes at the base of the Hirnantian reported in several paleocontinents [Marshall and Middleton, 1990 ; Middleton *et al.*, 1991] were introduced into the general discussion by Brenchley *et al.* [1994] : they interpreted the positive excursion of $\delta^{13}C$ at the base of the Hirnantian as a consequence of the sudden increment of organic productivity and/or carbon sedimentation. This increment would eventually have lowered the level of atmospheric CO_2, producing an icehouse effect. By means of a series of experiments with general circulation models, Gibbs *et al.* [1995] pointed out that a decrease of the CO_2 level until 10x present values would be enough to explain the known snow covered surface and the short duration of the late Ordovician glaciation.

However, CO_2 concentration should have been lower than the one mentioned above if some of the parameters considered in the postulated models had not been as extreme as those envisaged : e.g., there is sedimentary and faunistic evidence to suggest that the North Gondwana margin would not have been adjacent to the South Pole during late Ashgill times as considered therein. According to the paleogeographic reconstructions suggested by Beuf *et al.* [1971], Robardet and Doré [1988], Brenchley *et al.* [1991], Paris and Robardet [1990] and Astini [1999], and also to sedimentological and paleoecological evidence from the remnants of the northern Gondwana margin [Vennin *et al.*, 1998], the late Ashgill South Pole would have been close to the present Guinea Gulf, more than 2,000 km towards the interior of emerged land. As a result, a model explaining the fall of CO_2 levels even below those predicted in the experiments of Gibbs *et al.* [1995, 1997] seems necessary.

Kump *et al.* [1999] proposed a new hypothesis suggesting that an increment in silicate weathering during the late Ordovician (related to the Taconic orogeny) was the main cause of the long-term drawdown of atmospheric CO_2, directly inducing Hirnantian glaciation. The authors also explain the $\delta^{13}C$ positive excursion at the base of the Hirnantian as a consequence of the weathering of carbonate platforms during the Hirnantian sea-level lowstand. Nevertheless, the model fails to explain the end of the glaciation since its forcing factor, the weathering after the orogeny, presumably would have continued through the Silurian, as Kump *et al.* [1999 : p. 184] themselves recognize. This is an important limitation for the weatherability hypothesis since geological evidence of global Silurian glaciations is absent. Data from South America on the existence of Llandovery diamictites [Grahn and Caputo, 1992 ; Grahn and Paris, 1992] could be better explained as the product of local mountain glaciation according to Hambrey [1985, p. 282]. In addition, according to the $^{87}Sr/^{86}Sr$ strong decrease from the Cambrian to the Upper Ordovician rocks recorded by Veizer *et al.* [1999], it can be concluded that mountain uplift and weathering decreased as well during the Ordovician, diminishing also plausibility of the weatherability hypothesis by Kump *et al.* [1999].

If the coincidence of Hirnantian glaciation and high levels of greenhouse gases seems a paradox, another further perplexing phenomenon is the fact that glaciation suddenly succeeded a climatic amelioration on the northern Gondwana margin, whose platforms are dispersed across southwestern Europe and North Africa. In this region, glaciation took place immediately after deposition of disconnected temperate bioclastic limestones and pelmatozoan-bryozoan mud-mounds [Vennin *et al.*, 1998], of 0.1-300 m thick, and overlying several thousand meters of Lower-Middle Ordovician siliciclastic sediments. The latter represent temperate to cold environments which predominated during ca. 70 m.y. and lack distinct episodes of carbonate production. In this paper, we document and discuss evidence that the sharp Ashgill climatic amelioration of the Mediterranean region and the abrupt onset of a short glaciation period were directly related. A preliminary discussion of the proposed hypothesis was presented in Villas *et al.* [2001].

OUTLINE OF THE GEOCHEMICAL CYCLE OF CARBON

The burial of carbonate is well known as the most important CO_2 sink on earth and responsible for about 80 % of the carbon deposited on the ocean floor [Berner and Lasaga, 1989]. The carbon dioxide can be taken from the atmosphere during the weathering of silicate rocks, a process introduced by Berner *et al.* [1983], Berner and Lasaga [1989], Berner [1991] and Berner and Kothavala [2001] in their computer models of the geochemical carbon cycle as the main carbon flux from the atmosphere to the ocean. This process was also considered by Kump *et al.* [1999] as the main forcing factor of glaciation. However, there is also a direct flux of carbon from the atmosphere to the oceans by means of CO_2 dissolution, producing bicarbonate ions and eventually precipitation of carbonates [Bakwin, 1999]. The concentration of dissolved CO_2 in seawater depends on the partial pressure of CO_2 in air. The direct flux of carbon from the atmosphere to the oceans is considered by far the most important of all the fluxes of the natural carbon cycle

[Holser *et al.*, 1988 ; Faure, 1991 ; Tans, 1998]. As a result, it can be supposed that a strong increment of carbonate sedimentation and subsequent burial would reduce the concentration of bicarbonate ions in the seawater [$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$]. Subsequently, the lowering in the concentration of bicarbonate ions will lower the concentration of the dissolved carbon dioxide [$CO_2\,(aq) + H_2O \rightarrow H^+ + HCO_3^-$, where CO_2 (aq) is the dissolved CO_2]. Eventually, more carbon dioxide will be taken from the atmosphere by dissolution, until a new equilibrium dependent on the partial pressure of CO_2 in air is reached, leading to a significant impoverishment of that gas in the air.

According to the natural processes of the geochemical carbon cycle, it is possible to evaluate the CO_2 mass extracted from the ocean during a period of time, estimating the mass of carbonate buried during that time in a similar way to that followed by Budyko and Ronov [1979], Ronov [1980] and Hay [1985] in their studies of the carbonate and CO_2 accumulated during the whole Phanerozoic. In this way, it can be directly tested if an extra-amount of carbonates deposited during the late Ordovician can account for the predicted lowering of atmospheric CO_2 levels during the same epoch : from 14-18x present atmospheric level during most of the Ordovician [Berner, 1994 ; Yapps and Poth, 1992 ; Berner and Kothavala, 2001] to 10x present atmospheric level during the Hirnantian [Gibbs *et al.*, 1997], or even lower values.

THE LATE ORDOVICIAN CARBONATE SEDIMENTATION

An important amount of carbonates were deposited during late Ordovician times in some regions previously characterized by predominantly siliciclastic sedimentation and/or emerged lands. If this extra-sedimentation of carbonates (compared to the Ordovician average) was not accompanied by an increment of the CO_2 degassing due to igneous and metamorphic activities, the lowering in CO_2 that seemingly accompanied the Hirnantian glaciation could broadly be estimated. This premise seems certainly adequate in view of the decline in volcanic activity described for the late Ordovician [Kump *et al.*, 1995], after the important volcanic outgassing associated with eruption of Caradoc bentonites along the magmatic arc of eastern Laurentia [Huff *et al.*, 1992, 1993 ; Lavoie, 1995]. Although a global evaluation of the whole Upper Ordovician carbonates recorded all over the world is beyond the scope of this work, we can propose a preliminary approximation by estimating the carbonate mass deposited during that time span in two key regions where the increment in carbonate sedimentation was particularly important : the northern Gondwana margin and Laurentia. These two areas are considered as key representatives of the whole late Ordovician carbonate platforms, but further global estimates of the total increment in carbonate sedimentation during this time span must be made to test and refine the proposed model.

North Gondwana

A drastic change from siliciclastic to carbonate-dominated sedimentation took place during earliest Ashgill times on the platforms bordering the northern Gondwana margin, which went on until the Hirnantian glacioeustatic drop. The thickness of these carbonates is generally not significant, but their lateral distribution was important. The extent of this carbonate platform is evidenced by the occurrences of Ashgill bioclastic limestones and dolostones in the Iberian Peninsula [Hafenrichter, 1979], the Armorican Massif [Paris *et al.*, 1981], the southern Montagne Noire [Havlíček, 1981], Sardinia [Leone *et al.*, 1991], the Carnic Alps [Dullo, 1992 ; Schönlaub, 1988 ; Serpagli, 1967 ; Vai, 1971], Thuringia [Ferretti and Barnes, 1997 ; Knüpfer, 1967] and Libya [Bergstrom and Massa, 1991 ; Buttler and Massa, 1996]. The lateral extent of the carbonate margin suggested by these remnants would extend across more than 2,000 km. A N-S transect would reach at least 1,200 km, considering its relics in Central Europe (southern Germany, Carnic Alps) and North Africa (Libya), and even ignoring the superposed Hercynian tectonic shortening. Thus, the total surface of the carbonate platform on the northern Gondwana margin can be estimated as 2.4×10^6 km^2 as a minimum.

The evaluation of the average thickness of carbonates deposited on this margin is difficult as the thickness of the sedimentary successions is extremely variable, and some of those carbonates were totally eroded during the Hirnantian low-stand (fig. 1). The lowest thickness corresponds to the Kalkbank Limestone of Thuringia (Germany), which is only 0.1-0.4 m thick [Ferretti and Barnes, 1997 ; Knüpfer, 1967], and the highest one to the Laquiana Limestone of north-western Spain which reaches a thickness of up to 300 m [Pérez Estaún, 1978]. Between both extreme values, thickness ranges from 10-100 m of the Djeffara Formation in Libya [Buttler and Massa, 1996], nearly 60 m of limestones of an unnamed unit overlying the Bryozoan Shales in north-western Anatolia [Sayar, 1984], 6-20 m of the Wolayer and Uggwa limestones in the Carnic Alps [Schönlaub, 1998], up to 20 m of calcareous mudstones with thin encrinitic and micritic limestone beds of the Punta S'Argiola Member of the Domusnovas Formation [Ferretti and Serpagli, 1991] and up to 50 m of marls and limestones of the Tuviois Formation [Loi, 1993] in Sardinia, more than 7 m of massive bioclastic limestones at the top of the Rosan Formation in the Armorican Massif [Paris *et al.*, 1981], and up to 50 m of bioclastic limestones changing laterally into 12-25 m of marls and limestones in northeastern Spain [Hammann, 1992 ; Vennin *et al.*, 1998]. According to these greatly variable thicknesses, an average thickness for the complete carbonate deposits can be estimated to be at least 10 m. This estimate is very conservative considering the thicknesses listed above, but it is adequate because some carbonates display incomplete mixtures with siliciclastic sediments.

According to the evaluation of the extent of the North Gondwana platforms (2.4×10^6 km^2), and the estimated average of the carbonate thickness (10 m), the approached total volume of pure carbonate accumulated in the region during the pre-Hirnantian Ashgill would be 24×10^{12} m^3. Considering the mean density of limestones, 2,550 kg/m^3 [Telford *et al.*, 1990], the mass of the total carbonate volume would be about 60×10^{15} kg. In this estimate the fact that some of the original limestones were transformed into dolostones during the glacioeustatic Hirnantian fall or subsequent hydrotermal processes during the Hercynian and Alpine orogenies is ignored. The changes of volume in the

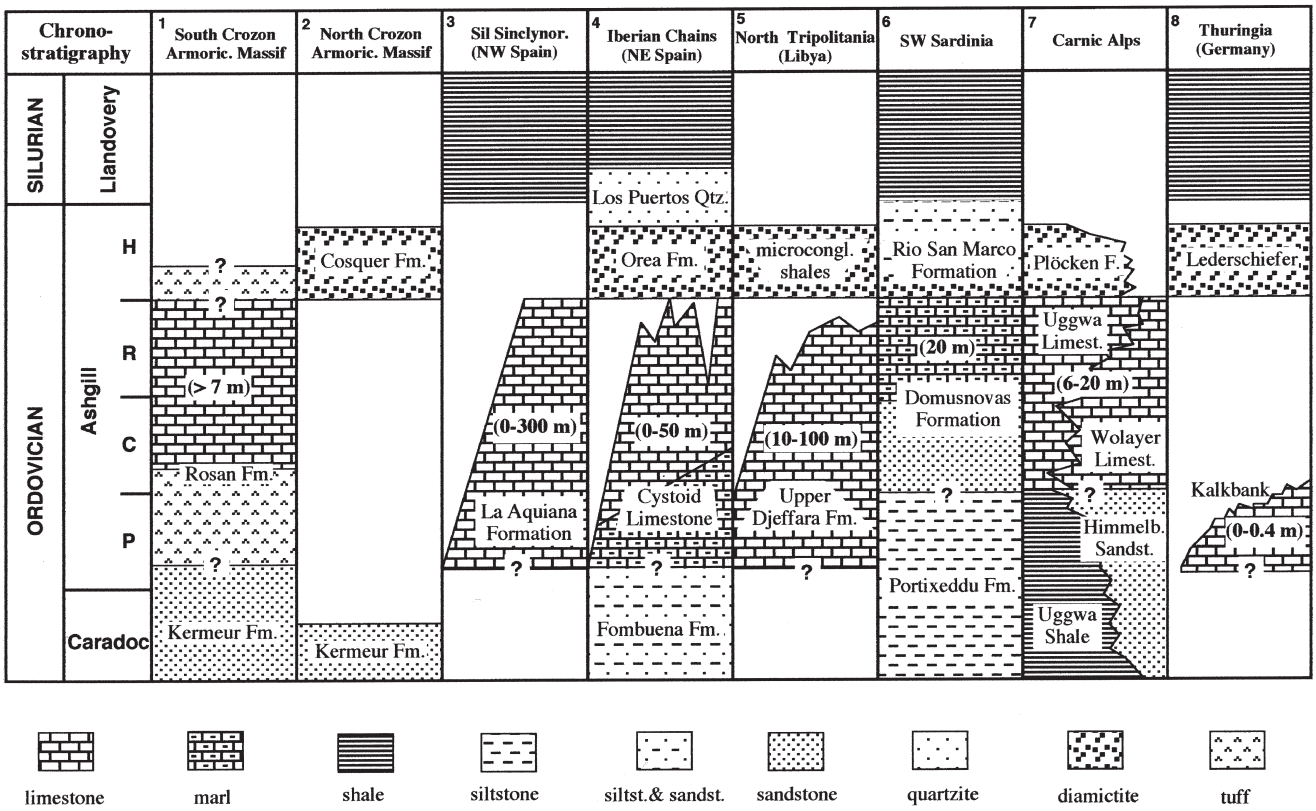

FIG. 1. – Suggested correlation of the Ashgill limestone units from selected regions of the northern Gondwana platforms, based on original stratigraphic columns by Paris *et al.* [1981] and Mélou [1987] (1), Robardet and Doré [1988] (2), Gutiérrez-Marco *et al.* [2002] (3), Vennin *et al.* [1998] and Gutiérrez-Marco *et al.* [2002] (4), Buttler and Massa [1996] (5), Leone *et al.* [1991] (6), Schönlaub [1998] (7), and Ferretti and Barnes [1997] (8).

FIG. 1. – Proposition de corrélation des unités calcaires d'âge ashgill à partir de différents domaines choisis sur la partie nord de la plate-forme gondwanienne et basée sur les travaux de stratigraphie de Paris et al. *[1981] et Mélou [1987]* (1), *Robardet et Doré [1988]* (2), *Guttiérrez-Marco* et al. *[2002]* (3), *Vennin* et al. *[1998] and Guttiérez-Marco* et al. *[2002]* (4), *Buttler et Massa [1996]* (5), *Leone* et al. *[1991]* (6), *Schönlaub [1998]* (7), *et Ferretti et Barnes [1997]* (8).

original limestones due to these processes would have been minimal and are not considered in the above estimates.

Although the weathering process of silicates is not regarded herein as the main CO_2 sink during the late Ordovician, the reactions below which describe this process are useful to calculate the equivalence between the mass of atmospheric CO_2 and the mass of sedimented carbonates

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \quad [1]$$

$$MgSiO_3 + CO_2 \rightarrow MgCO_3 + SiO_2 \quad [2]$$

Applying stoichiometry, a mass of 440 gr of CO_2 corresponds to 1,000 gr of $CaCO_3$.

According to the above calculations, a minimum CO_2 mass of 26×10^{15} kg (59×10^{16} mol) buried in the northern Gondwana platforms during Ashgill times due to carbonate sedimentation can be estimated. This is about 10 times the present mass of CO_2 in the atmosphere reported as 2.43×10^{15} kg (5.5×10^{16} mol) by Khalil [1999]. Thus, despite the reduced estimated surface of the northern Gondwana carbonate margin and the conservative estimate of the average carbonate thickness, the CO_2 mass buried during the pre-Hirnantian Ashgill reaches a remarkable magnitude, enough to be considered when analyzing a possible late Ordovician alteration of the carbon cycle.

Laurentia

Laurentia is another site where a sudden change from siliciclastic to carbonate sedimentation took place during the late Ordovician and, as suggested below, could have favoured a sharp increase in carbonate sedimentation. The sedimentary turnover coincided with the highstand sea-level patterns that flooded the North American cratonic platforms, reported as the most extensive flooding event recorded in the Paleozoic for North America [Ross and Ross, 1995]. Much of those deposits, Cincinnatian (late Caradoc-Ashgill) in age, consist of dolostones, especially across widespread areas of the Canadian Shield, which completely covered the Transcontinental Arch [Ross, 1976].

The extraordinary transgression that started in the Mohawkian but reached its maximum in the Cincinnatian permitted that, at least, a surface of 6.5 x 10^6 km^2 changed from being emerged or under siliciclastic sedimentation during the Mid Ordovician to a continuous carbonate productivity leading to thick successions of dolostones and limestones [see correlation chart by Ross *et al.,* 1982]. This surface has been estimated according to the paleoenviromental maps of Ross [1976] and Elias [1991]. However, the Laurentian carbonate surface could even be 50 % larger as these authors did not include in their studies the

Canadian Arctic and Greenland, which also suffered the Cincinnatian transgression [Jin, 1999]. Nevertheless, we prefer to make a conservative estimate because, during the highstand, some regions previously under carbonate sedimentation, as those peripheral to the North American craton, changed into siliciclastic sedimentation. This is also true for the Quebec Basin, affected by the Queenston delta complex, related to the Taconic Orogeny [Barnes *et al.*, 1981]. The areal loss of carbonate production in the peripheral sites would approximately compensate the infravaloration of areal increment of carbonate sedimentation on the craton. Obviously, more precise estimates of this areal increment will allow refining the evaluation on the extra-burial of CO_2 presented below.

The thicknesses of the Cincinnatian carbonate successions from North America are much higher than those reported above for the northern Gondwana Ashgill. Most of the pre-Hirnantian Cincinnatian reference successions across North America are thicker than 100 m : e.g., the Hanson Creek Formation in Nevada [166 m thick ; Merriam, 1940], the Ely Spring Dolomite in Nevada and Utah [150 m thick ; Droser and Sheehan, 1995], the Drakes and Ashlock Formations in central Kentucky [more than 120 m thick ; Weir *et al.*, 1984], the Red River and Stony Mountain Formations in the Willinston Basin (more than 180 m thick), the Montoya Group in southern New Mexico and westernmost Texas (130 m thick), and the Beaverfoot Formation in British Columbia and Alberta (120 m thick) [Elias, 1991]. Thus, an average thickness for the pre-Hirnantian Cincinnatian carbonates on the North American craton of at least 100 m can be estimated. According to the above estimate of surface (6.5×10^6 km^2), the total volume of carbonates would reach at least 650×10^{12} m^3.

Simplifying the problem, we consider that limestones and dolostones were in about equal proportions within that carbonate volume. Considering also a density of 2,630 kg/m^3 for the mixture of dolostone + limestone [Telford *et al.*, 1990], a total mass for those carbonates of 1,710 $\times 10^{15}$ kg can be calculated. Following the stoichiometric laws, the molecular weights of both CO_2 and of a mixture of $CaCO_3$ + $MgCO_3$, and considering the above reactions [1] and [2], 48 % of that carbonate mass (816×10^{15} kg = 18.5 $\times 10^{18}$ mol) may represent the CO_2 mass buried on the Laurentia epicontinental seas during the Cincinnatian. This extra-burial of CO_2, equivalent to about 335 times the present values of atmospheric CO_2, and much more important than the estimated burial for the northern Gondwana platforms during the pre-Hirnantian Ashgill, should have greatly altered the equilibrium between the CO_2 dissolved in the oceans and the partial pressure of CO_2 in the air, eventually causing an important reduction of the latter.

THE FORCING FACTORS OF THE CARBONATE SEDIMENTATION ENHANCEMENT

Even accepting that the main sink of the atmospheric CO_2, which eventually induced the Hirnantian glaciation, is represented by the Upper Ordovician carbonate rocks of North Gondwana and Laurentia, it is still necessary to identify the forcing factors that conditioned such an important change in sedimentation patterns. Although a precise analysis of these factors is not intended here, we describe a possible scenario interrelating different phenomena that eventually led to the optimal environmental conditions for the sedimentation of an important carbonate mass in a short time interval.

The late Ordovician transgression

It is implicit in the proposed model that the early Cincinnatian transgression that flooded the North American craton was one of the main forcing factors. The transgression, which started during the early Caradoc and progressed until the well-established Hirnantian fall of the sea level, is globally recognized in different paleocontinents, such as Baltica, Laurentia and Gondwana [see a summary in Brenchley *et al.*, 1994]. The transgression could mainly be related to increments in plate accretion, since there is no evidence of Middle Ordovician continental ice caps responsible for a subsequent sea-level rise under warming conditions. The main effects of the sea-level rise can be recognized in the lower Ashgill deposits of North Gondwana as the beginning of an important carbonate productivity, and the generalized immigration of subtropical faunas [Havlíček, 1981 ; Villas, 1985 ; Hammann, 1992].

The latitudinal position of the North Gondwana platforms

The widely admitted equatorial location of Laurentia during the Ordovician accounts for the optimal temperature conditions for carbonate deposition. In addition, the latitudinal position of the northern Gondwana platforms should also have been adequate for carbonate sedimentation (fig. 2). The facial features of the limestones described by Hafenrichter [1979], Dullo [1992] and Vennin *et al.* [1998] can hardly be understood in latitudinal positions close to 80º S, as suggested by some paleogeographic reconstructions [Scotese and McKerrow, 1990]. A high-latitude setting fits in well with siliciclastic sedimentation and low-diverse faunistic associations that thrived in the region during early and mid Ordovician times, but contrast with the development of carbonate sedimentation. According to an actualistic oceanographic configuration, a latitude up to 50º S for the northern Gondwana platforms would make the arrival of warm subequatorial currents possible. But the latitude could have been even lower than this, considering that a faster spinning earth during the Ordovician would have generated a displacement toward the equator of subtropical high-pressure and temperate low-pressure zones, affecting the course of the oceanic currents [Christiansen and Stouge, 1999].

A continental mass placed at intermediate latitudes, to the northwest of the northern Gondwana margin, could have deflected southward the South Equatorial current, enabling it to reach the margin. The envisaged paleogeographic reconstruction strongly resembles the present geography of the South Pacific, where Australia deflects the warm South Equatorial current towards New Zealand [Nelson *et al.*, 1988 ; Whalen, 1995]. This deflection leads to the present sedimentation of briomol/bryonoderm-type, non-tropical limestones on the shelf surrounding these islands at latitudes 45-50º S [Nelson *et al.*, 1988] and has contributed episodically to warm and wet conditions in southern Australia and New Zealand [McGowran *et al.*, 1997]. The continental mass that could have deflected an equivalent South Equato-

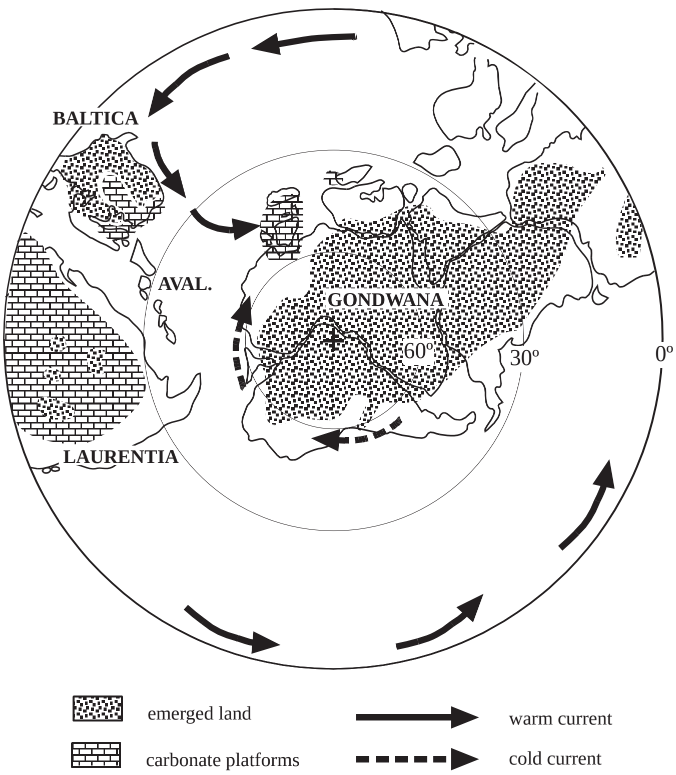

FIG. 2. – Distribution of the major carbonate platforms during the late Ordovician (*ca.* 445 Ma.) in the southern hemisphere. Palaeogeographic map according to reconstructions of Ross [1976], Erdtmann [1982], Neuman and Harper [1992], Vennin *et al.* [1998] and Gutiérrez-Marco *et al.* [2002].

FIG. 2. – *Répartition des principales plates-formes carbonatées au cours de l'Ordovicien terminal (445 Ma) dans l'hémisphère sud. Carte paléogéographique selon les reconstitutions de Ross [1976], Erdtmann [1982], Neuman et Harper [1992], Vennin* et al. *[1998] et Guttiérrez-Marco et al. [2002].*

rial current during Ashgill times toward North Gondwana could be identified as Baltica, after the accretion of Avalonia. Warm subtropical ocean waters, generated in sub-equatorial latitudes, would flow southward along the eastern coasts of Baltica and, therefore, its supposed subequatorial position could well have enabled it to play the oceanographic role of the present Australia (fig. 2). The proposed deflection of a warm current towards the northern Gondwana margin would simultaneously account for the sudden and massive immigration of a distinct benthic fauna previously restricted to Baltica and Laurentia [Hammann, 1992], such as the brachiopod *Nicolella* community [Havlíček, 1981].

The increase in oceanic circulation and nutrient input

An adequate influx of nutrients is an important ecological control over the proliferation of life and carbonate productivity in the oceans [Hallock *et al.*, 1988]. Calcium and magnesium are among the most important elements controlling the deposition of late Ordovician carbonates. Upwelling of waters saturated in $CaCO_3$ and rich in nutrients increases the rate of carbonate production and preserves cold-water carbonates [Prasada Rao, 1981]. Such an increment in the influx of nutrients was suggested by Brenchley *et al.* [1994] for the early Hirnantian, as a result of an increase in the circulation of cold bottom waters and upwelling. However, even accepting the general model proposed by these authors, the precise timing can be discussed and the process anticipated. According to Wilde [1991], the Upper Ordovician upwelling would have been promoted by the development of sea ice that initiated cold down-welling currents in the polar region. This author relates the enhancement of oceanic circulation with the known facies succession in Dob's Linn (Scotland), pointing out the sedimentary change from anoxic black shales during pre-Ashgill times to more oxidized muds during the late Ordovician. Accordingly, in this peripheral site of the tropical Laurentia, the ventilation of middle depths by vertical advection would have been initiated in Ashgill times, coinciding with the first deposits of the lower Ashgill Upper Hartfell Shale [the *complanatus* biozone, Barnes and Williams, 1988]. The strong increment of oceanic circulation is also recognized during early Ashgill in the North Gondwana margin with the record of carbonate sedimentation. The large volumes of organic matter that must have accompanied the enhancement of oceanic circulation and biogenic carbonate production were not buried in this region ; neither do they appear to be an important part of the preserved early Ashgill global sedimentary record. Consequently, their contribution to a long-term drawdown of CO_2 during this period, in comparison with that of the carbonate sedimentation CO_2 sink, must have been small.

THE EMERSION OF THE CARBONATE PLATFORMS AND THE END OF THE GLACIATION

The proposed model, relating the Hirnantian glaciation to the CO_2 sink on widespread Ashgill carbonate platforms, carries an implicit mechanism eventually marking the end of the glaciation after a short time-span. The glacioeustatic lowering of the sea level during glaciation made the sea retreat from the platforms, stopping carbonate sedimentation and closing the CO_2 sink. In fact, the glacioeustatic lowering of the sea level and the closing of the carbonate sedimentation CO_2 sink are so intimately related that the described mechanism would never have triggered a steadily progressing glaciation. If the CO_2 sink caused by carbonate sedimentation and the concomitant lowering of temperature were lineally correlated with ice cap growth and glacioeustatic sea-lowering, both phenomena would be mutually controlled and glaciation could never have progressed in this way. However, the model works if both phenomena were not lineally correlated and the temperature lowered very quickly after attaining a certain CO_2 threshold [as suggested by Gibbs *et al.*, 1997], triggering the quick growth of the ice cap.

Once the ice cap started to grow and the global regression to advance, a second CO_2 sink would have started to function, feeding back the glaciation and making it progress more rapidly. The second sink would be related to the weathering of carbonates, previously deposited, which were emerging with the global regression. This CO_2 sink was already envisaged by Kump *et al.* [1999] among other positive feed-backs of the Hirnantian glaciation. The emersion that led to the weathering and karstification of the carbonate platforms is well known from different paleocontinents [Carls, 1975 ; Brenchley and Newall, 1980]. The weather-

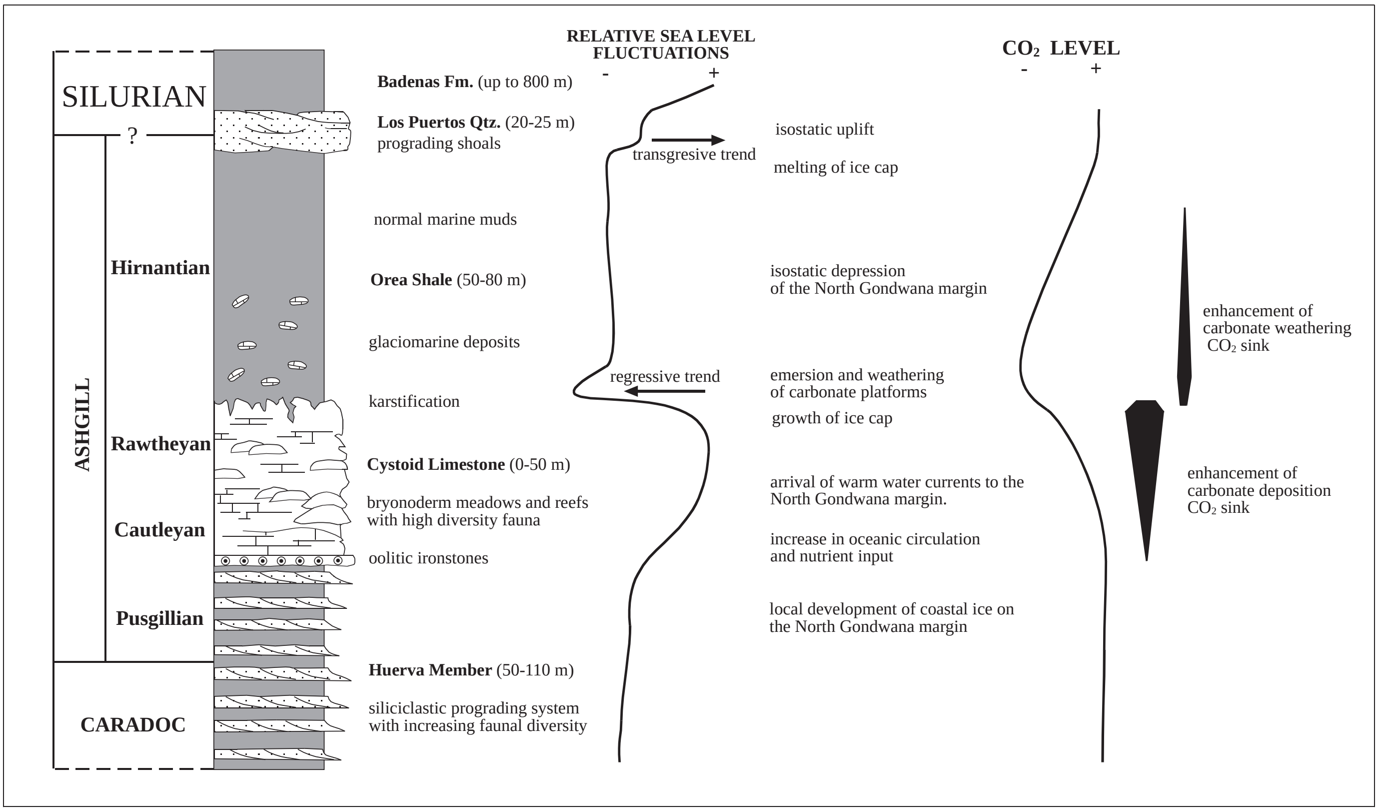

FIG. 3 – Upper Ordovician succession in the Iberian Chains (NE Spain), with environmental, oceanographic, climatic and atmospheric interpretations. The relative sea level curve responds in general to global eustatic fluctuations, but is also affected by isostatic phenomena of the northern Gondwana margin.
FIG. 3. – Succession de l'Ordovicien supérieur dans les Chaînes ibériques (NE Espagne), et interprétations environnementales, océanographiques, climatiques et atmosphériques. La courbe de variations relatives du niveau marin répond en général à des fluctuations eustatiques mais est également affectée par des phénomènes isostatiques sur la marge nord du Gondwana.

ing of carbonate works only as a short-term CO$_2$ sink [Berner and Lasaga, 1989], but it would have been enough to enhance the CO$_2$ uptake during the early Hirnantian when the platforms began to emerge, accelerating the glaciation. As the glaciation advanced, this enhancement of carbonate weathering would have decreased with the fall of the average temperatures and of the atmospheric partial pressure of CO$_2$, also decreasing its importance as a CO$_2$ sink.

Finally, with the carbonate sedimentation CO$_2$ sink almost totally closed due to the glacio-eustatic regression and the carbonate weathering CO$_2$ sink attenuated, volcanic and metamorphic CO$_2$ degassing would have equalled and surpassed the atmospheric CO$_2$ uptake, allowing a recovery of pre-glacial CO$_2$ levels, the raising of average temperatures, and the melting of the ice-cap. After this melting, oceanic circulation did not recover pre-Hirnantian Ashgill strength, resulting in a strong stratification of ocean waters and precluding the recovery of the extensive carbonate deposition.

On the other hand, the $\delta^{13}C$ strong positive shift during the early Hirnantian was interpreted by Brenchley *et al.* [1994] as a consequence of a sudden increment in productivity and/or sedimentation of organic carbon. Certainly, burying of this supposedly increased mass of organic carbon would have been necessary to account for a long-term alteration in the carbon cycle. However, the Hirnantian stratigraphic record is not especially characterized by high organic carbon contents. Although positive shifts in $\delta^{13}C$ are usually related to increments in production and burial of organic carbon, the early Hirnantian shift has been interpreted as the expected response to increased rates of carbonate-platform weathering during glacioeustatic sea-level lowstands [Kump *et al.*, 1999], an interpretation accepted herein. Finney *et al.* [1999] also explain the early Hirnantian positive shift in $\delta^{13}C$ as the result of glaciation and sea level fall. The carbon isotope fractionations associated with the precipitation of carbonate are small, but can raise the $\delta^{13}C$ of carbonates about 1 per mil above that of the dissolved HCO_3^- [Karhu, 1999]. The weathering and dissolution of the widespread carbonate platforms that emerged during the Hirnantian glacioeustatic event would have relatively enriched the marine shallow waters in ^{13}C. This would ultimately have influenced the $\delta^{13}C$ of the marine carbonates [as those analyzed by Kump *et al.*, 1999 ; Kaljo *et al.*, 1999, 2001], as well as the $\delta^{13}C$ of the calcite shells of the organisms thriving in those environments, as displayed by the Hirnantian brachiopods analyzed by Brenchley *et al.* [1994]. The synchronous rise in both oxygen and carbon isotope curves [Brenchley *et al.*, 1994 ; Heath *et al.*, 1998] supports the above explanation, since ice growth is also expected to be synchronous with sea-level lowering and the start of the weathering of carbonate platforms.

DISCUSSION AND CONCLUSIONS

A model relating the sharp Ashgill climatic amelioration reported in the Mediterranean region (related to broad carbonate deposition) and the abrupt onset of a short glaciation episode is proposed in this paper (see fig. 3). The onset of the latter is explained as a result of the accumulation of great volumes of carbonates during the pre-Hirnantian late Ordovician, in regions where these deposits were previously absent. These carbonates are considered as the sink of the atmospheric CO_2, which was extracted from the late Ordovician atmosphere, causing a remarkable lowering of its values at the beginning of the Hirnantian. This model follows Brenchley *et al*. [1994] in considering that the Hirnantian glaciation was intimately related to changes in the carbon cycle, but differs from these authors in the sink considered for the atmospheric CO_2. Brenchley *et al*. [1994] proposed an earliest Hirnantian increment in production and/or sedimentation rates of organic carbon as the major sink for the atmospheric CO_2. In contrast, an alternative hypothesis is proposed herein, in which the main sink for the atmospheric CO_2 would be the carbonate sedimentation throughout the pre-Hirnantian late Ordovician. The estimated mass of CO_2 buried in the Laurentia and the northern Gondwana platforms during the pre-Hirnantian late Ordovician, nearly 350 times the present values of atmospheric CO_2, is important enough to have greatly altered the equilibrium between the CO_2 dissolved in the oceans and the partial pressure of CO_2 in the air, eventually causing an important reduction of the latter.

The new hypothesis on the triggering factor of the Hirnantian glaciation agrees with that by Kump *et al.* [1999] on the timing of the forced extraction of atmospheric CO_2, shifting it from the early Hirnantian to late Caradoc-early Ashgill times, although it radically changes the main CO_2 sink from silicate weathering to carbonate sedimentation. While the weatherability hypothesis of Kump *et al.* [1999] fails to explain the end of the glaciation, since the corresponding CO_2 sink presumably would have remained open throughout the Lower Silurian, the new carbonate sedimentation hypothesis offers a simple explanation for the end of the glaciation. The glacioeustatic lowering of the sea level, concomitant with the glaciation, would have stopped the extra sedimentation of carbonate due to the retreat of the oceans from the platforms, closing this CO_2 sink simultaneously with the development of the ice cap. The pre-glacial CO_2 levels would then have been recovered, due to the volcanic and metamorphic CO_2 outgassing. After the subsequent melting of the ice cap, the oceanic circulation did not recover the pre-Hirnantian Ashgill strength, resulting in a strong stratification of ocean waters and precluding the recovery of an extensive carbonate deposition.

Further studies should analyze the forcing factors and the timing of the development of coastal ice on the northern Gondwana platform across the Caradoc-Ashgill transition, since this seems to have triggered the increase in oceanic circulation that greatly enhanced the Ashgill carbonate sedimentation.

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