Polarforschung 59 (3): 179–198, 1989 (erschienen 1991)

Mineralogical and Geochemical Characterization of the Ameghino Formation Mudstones (Upper Jurassic, Antarctic Peninsula) and Its Stratigraphical, Diagenetical and Paleoenvironmental Meaning

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Summary: As a result of a petrographical, mineralogical and geochemical characterization of the Ameghino Formation mudstones (Upper Jurassic-Lower Cretaceous, Antarctic Peninsula), „epiclastic" radiolaria-rich and mixed (radiolaria-rich + tuff) mudstone types were recognized. Contents of clastic material in the mudstones generally increase with younger paleontological age, but local exceptions to this trend have been found.The anoxic environment of the lower part of the sequence changes to more oxidizing conditions towards the top, in transition to the Hauterivian - Barrêmian conglomerates. Element to element correlations show good agreement with the normal dlfferentiation trends of volcanic (andesite - rhyolite) rocks, suggesting that the overall sequence is mainly volcanic in origin with various grade of reworking. For example, the radiolaria-rich mudstone matrix could have been originated from very fine touffaceous suspensions deposited very slowly after the main fall of the tuffs. However, in the upper part of the sequence, some epiclastic supply is revealed by petrographic evidence and illite crystallinity index. The clay mineral association (illite, chlorite and illite-smectite mixed layers) is mainly of diagenetic origin in the stratigraphically lower sections. Low percentages of expendable layers in the illite-smectite mixed layers, as well as the general mineralogical association, suggest a late mesodiagenetic stage, and together with geological evidence, a relatively deep burial (> 1000 m - probably > 2500 m) and temperatures exceeding 100° C.

Zusammenfassung: Anhand petrographischer, mineralogischer und geochemischer Untersuchungen von Tonsteinen der Ameghino-Formation (oberer Jura - untere Kreide, Antarktische Halbinsel) wurden radiolarienreiche, „epiklastische" und gemischte (radiolarienreich + tuffitisch) gefunden. Der klastische Anteil der Tonsteine steigt im allgemeinen mit jüngerem paläontologischen alter: einige Ausnahmen von dieser Regel treten auf. Im Übergang Hauterive - Barrême wechselt das anoxische Milieuim im unteren Abschnitt zu eher oxischen im oberen Teil der Sequenz. Die Korrelationen der Elemente zeigen gute Übereinstimmung mit der normalen Differentiation vulkanischer Gesteine (Andesit-Rhyolit) und legen in der ganzen Sequenz einen hauptsächlich vulkanischen Ursprung mit unterschiedlich starker Aufarbeitung nahe. So wäre z.B. die Matrix der radiolarienreichen Tonsteine aus einer Suspension tuffitischen Materials bei sehr geringer Sedimentationsrate nach der Haupteruptionsphase der Tuffe entstanden. Petrographische Beobachtungen und ebenso die Illitkristallinität weisen jedoch auf geringen epiklastischen Eintrag im oberen Abschnitt der Sequenz hin. Die Mineralassoziation (Illit, Chlorit und Illit-Smectit-Wechsellagerungsminerale) im stratigraphisch unteren Abschnitt ist diagenetischen Ursprungs. Geringe quellbare Anteile in den Illit-Smectit-Wechsellagerungsmineralen, sowie die Mineralassoziation im allgemeinen, legen ein spät mesodiagenetisches Stadium und zusammen mit den geologischen Beobachtungen, eine relativ mächtige Überdeckung (> 1000 m, vermutlich > 2500 m) mit Temperaturen über 100° C nahe.

1. INTRODUCTION

The Ameghino Formation, also known as Nordenskjöld Formation, comprises a distinct sequence of radiolaria-rich mudstones and tuffs of Late Jurassic to Early Cretaceous age which are exposed on the north-eastern of the Antarctic Peninsula (Fig. 1a). The Ameghino Formation crops out at five localities along the eastern coast of the Antarctic Peninsula, but neither the base nor the top of the Formation can be observed anywhere. Intrusive contacts are the only stratigraphic relationship observed. The outcrops are situated between the Trinity Peninsula Group basement with its overlaying volcanic rocks to the north-west and uplifted Cretaceous sedimentary rocks to the south-east.

The Ameghino Formation is the oldest sedimentary unit in the north-eastern Antarctic Peninsula Basin, called Larsen Basin by MACDONALD et al. (1988). In this back-arc basin (MEDINA et al. in press) about 6000 m of epiclastic and volcaniclastic sediments were deposited from Late Jurassic to Early Tertiary times. During this time the Antarctic Peninsula was an active volcanic arc formed by the south-eastward subduction of proto-Pacific crust.

The situation of the Ameghino Formation at the base of the basin and its rich organic content makes it interesting as a potential source rock of hydrocarbon. In consequence the stratigraphy and the diagenetic history are important items to examine.

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Manuskript received: 15. 5. 90; accepted: 12. 10. 90

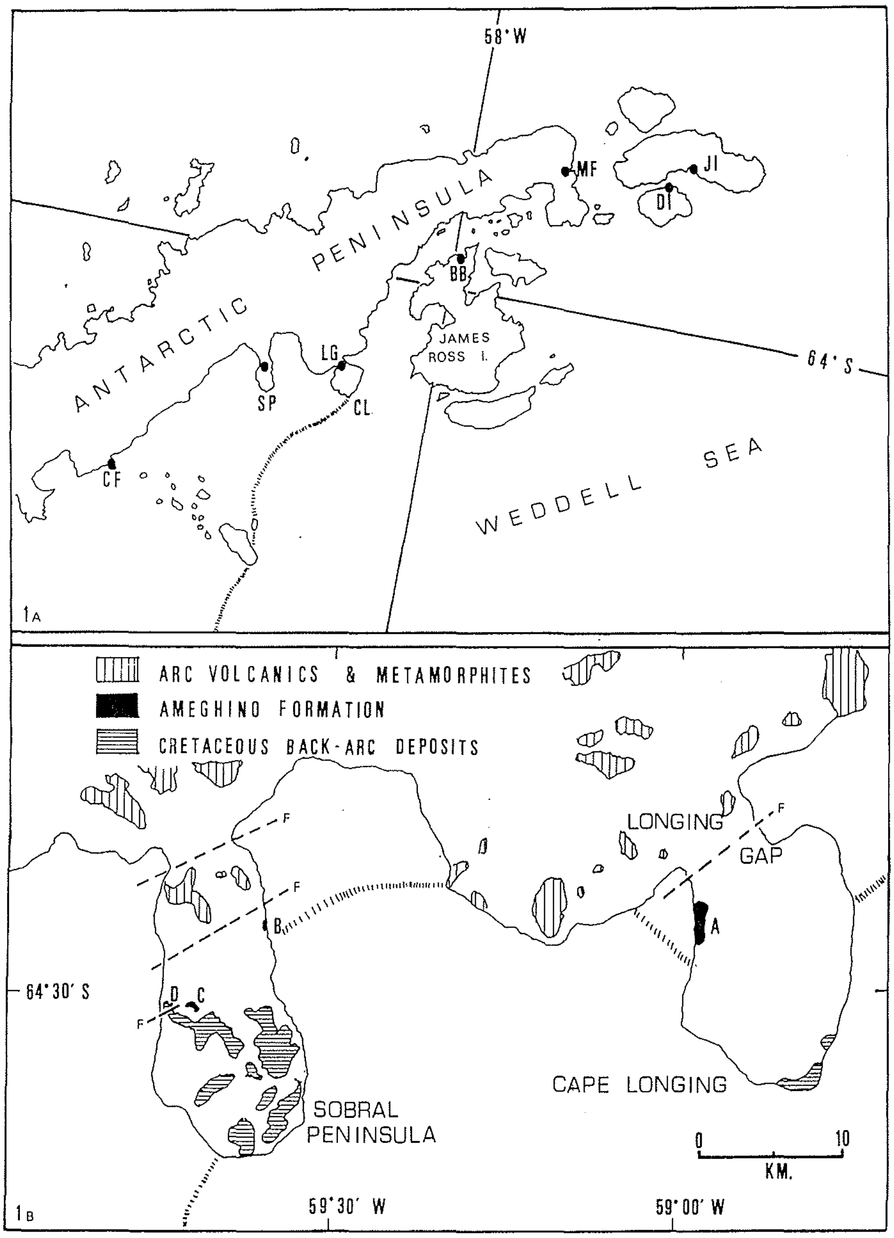

Fig. 1a: Sketch map of northern Antarctic Peninsula area showing the location of Ameghino Formation exposures (after FARQUHARSON 1983a). CF = Cape Fairweather, SP = Sobral Peninsula, LG = Longing Gap, CL = Cape longing, BB = Brandy Bay, MF = Mount Flora, DI = Dundee Island, JI = Joinville Island.

Abb. 1a: Skizze der Aufschlüsse der Ameghino Formation auf der nördlichen Antarktischen Halbinsel (nach FARQUHARSON 1983a).

Fig. 1b: Geological sketch map of Sobral Peninsula and Cape Longing showing the studied localities: A = Longing Gap (Longing section), B = Tres Amgios Nunatak (TA section), C = El Manco Nunatak ((Lower, Middle and Upper Sobral sections), D = SobC section.

Abb. 1b: Geologische Skizze der Halbinsel Sobral und Kap Longing mit den untersuchten Aufschlüssen.

In order to get new information on these subjects, mineralogical and geochemical studies have been carried out. New lithostratigraphic, paleoenvironmental and special diagenetic data are presented.

2. GEOLOGICAL SETTING AND PREVIOUS WORK

First studies on Ameghino Formation rocks were carried out by STONELEY & STANDREY (1952 and 1953, in FARQUHARSON 1983a) in the Longing region. ELLIOT (1966) and FLEET (1968) described similar rocks for the time in the Sobral Peninsula and at Cape Fairweather respectively. MEDINA & RAMOS (1981) adopted the name Ameghino Formation for these rocks, choosing the Longing Gap as the type locality (Fig. 1b). They also stated the Upper Oxfordian to Kimmeridgian age on the base of bivalve (mainly inoceramid) and ammonite content. New comments on the age of the fauna, including the El Manco Nunataks (Sobral Peninsula) were given by MEDINA et al. (1983).

The Ameghino Formation was later improperly named Nordensköld Formation by FARQUHARSON (1982, 1983a, 1983b). This author recognized the unit in several outcrops along the eastern coast of the Antarctic Peninsula (Fig. 1a). He described the rocks as radiolaria-rich mudstones and tuffs of Kimmeridgian - Tithonian to ?Lower Cretaceous age, deposited into an anoxic basin. A regional correlation with Upper Jurassic rocks of South Shetland, South Georgia, Patagonia and the South Atlantic Ocean was proposed too.

Although the Ameghino Formation is not exposed on James Ross Island, clasts of alternating mudstone and tuffs are abundant in the Lower Cretaceous sequence, showing marine vertebrates of Oxfordian - Berriasian age (OLIVERO et al. 1980); big glide blocks (INESON 1985) were interpreted as isolate exotic slabs transported to their present position by submarine sliding.

New observations concerning the stratigraphy and paleoenvironmental setting of the Ameghino Formation in Sobral Peninsula were carried out by DEL VALLE et al. (1988) and SCASSO & DEL VALLE (1989). A new stratigraphic division into Lower, Middle, and Upper Ameghino Formation in El Manco Nunatak is proposed (Fig. 2), pointing out differences to the type section sedimentology. Interbedded submarine volcaniclastic fan facies are described. The authors report the presence of a rich flora similar to that of the Mount Flora and tectonically highly deformed rocks not observed before. WHITHAM & STOREY (1989) studied the deformational history of these beds relating it to strike-slip deformation and the movement of the crustal blocks of West Antarctica. WHITHAM & DOYLE (1989) proposed a new stratigraphic division for this formation

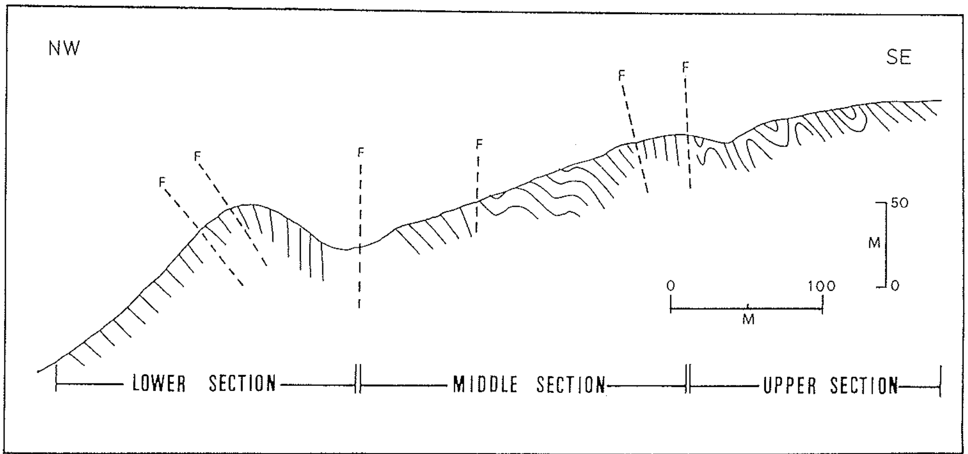

Fig. 2: Sketch of cross-section of El Manco Nunatak showing Lower, Middle and Upper Sobral sections on the Sobral Peninsula (after SCASSO & DEL VALLE 1989).

Abb. 2: Schematisches Profil durch die Sobral-Schichtfolge am El Manco Nunatak auf der Halbinsel Sobral (nach SCASSO & DEL VALLE 1989).

(following FARQUHARSON (1983 b) they call these rocks Nordensköld Formation). A lower member, the Longing member (Kimmeridgian - Thithonian), and an upper member, unfortunately named Amegino Member (Tithonian - Berriâsian) were defined at the Longing Gap. A third member, the Larsen Member (Berriasian) was defined on the eastern outcrop of the Sobral Peninsula (Tres Amigos Nunatak in this paper). In the western locality (El Manco Nunatak in this paper) they splitted the sequence into a first group with interbedded tuffs and mudstones characterizing the formation, assignated to their Ameghino Member, and into a second group of unfossiliferous mudstones and thick pebbly sandstones of unknown stratigraphic affinity (the last are the Upper Section and part of the Middle Section of SCASSO & DEL VALLE 1989, see Fig. 2).

Beginning with FARQUHARSON (1983 b) who considered them as facies variation of Ameghino (Nordenskjöld) rocks and ending with WHITHAM & DOYLE (1989) who put them out of the formation, the nature and stratigraphic position of the coarse intercalations of the Middle Section and the Upper Section are not clearly understood which is mainly due to the structural complexity. The Ameghino Formation rocks are faulted and slightly folded in the lower and middle sections, and they are folded in the upper section and in the Tres Amigos Nunatak. In the Longing Gap the beds are only gently inclined.

3. METHODOLOGY

As was discussed, sampling comprised different outcrops of the Ameghino Formation (Longing Gap, El Manco and Tres Amigos nunataks on Sobral Peninsula) which have undergone different diagenetic and tectonic processes. Outcrops of doubtful stratigraphic positions have also been sampled, like the Upper Section of El Manco Nunatak or the pelites from a small, isolated outcrop unterlaying the Barrêmian conglomerates, which is located west of the El Manco Nunatac (SobC section, Fig. 1b). The possible correlation between these rocks and the Upper Sobral section has already been discussed (SCASSO & DEL VALLE 1989). Though the contact is covered by debris, the mudstone beds show an attitude similar to that of the conglomerates, suggesting a probable concordant relationship.

One sample of a glide block with similar lithology and age as the Ameghino Formation included in the Lower Cretaceous sequence outcropping near the western coast of the Brandy Bay (north-western coast of James Ross Island), and a low grade metamorphic pelite of the Mount Flora Formation (Upper Jurassic to Lower Cretaceous continental beds), outcropping at the northern tip of the Antarctic Peninsula at Hope Bay, have been studied.

The samples from the El Manco Nunatak were collected following the stratigraphic scheme of SCASSO & DEL VALLE (1989): Samples SOB-01 to SOB-28 (from base to top of the Lower Sobral section); SOB-275 to SOB-45 (Middle Sobral section) and SOB-50 to SOB-66 (Upper Sobral section). The samples from the three outcrops of the Tres Amigos Nunatak (TA section) are named TA-1, TA-II and TA-III. Samples TA-OST, TA-MITTE and TA-WEST respectively belong to these outcrops. They are considered as samples without stratigraphic order, because the exact stratigraphic relations of these folded rocks are not clear. Samples SOB-C1, -C2 and -C3 originate from a small outcrop (SobC section) underlaying the Barrêmian - Hauterivian conglomerates. Samples FA-1 to FA-29 (base of top of Longing section) have been collected by Del Valle and Nunez for a paleomagnetic study. The samples from the glide block in James Ross Island (GD-1) and from Mount Flora (MF-1) have been collected by R. Scasso.

In general mudstones and calcareous concretional mudstones have been preferentially sampled. Petrographical observations on thin sections have been performed on most of the samples. Chemical analyses (Tab. 1) were made by means of X-ray fluorescence analysis (RFA) following the methodology proposed by PREISSINGER (1988). For detailed description of samples preparation see also SCASSO (1989) and GRUNENBERG (1989). The values obtained were calibrated with geostandards (GOVINDARAJU 1984, 1987) and corrected for matrix effects by a computer program. Loss of ignition has been determined by heating the sample at 100° C during one hour.

X-ray diffraction analyses have been performed on bulk, milled samples. Semiquantitative estimations have been made with help of the peak heights of one characteristic peak for every main mineral component. Thus the peak of 3.035 Å (quartz), 4.02 - 4.06 Å (plagioclase), 2.97 Å (alcaline feldspar), 3.035 Å (calcite), 1.63 Å (pyrite), 10

Å (illite), 7 Å (chlorite) and 12-15 Å (smectite) have been used. These measurements allowed a „stratigraphical comparison“ (i.e. between sample) in order to find out tendencies on a given section or to compare different sections (Tab. 1). Well defined peaks for alkaline feldspar and sanidine are found around 3 Å (STEWARD et al. in RIBE 1983). With raising calcium contents the plagioclase peaks are shifted to higher d spaces (BAMBAUER et al. 1967). Values for smectite and chlorite have been checked and corrected after special studies performed on the clay fraction and are only tentative. The virtual absence of kaolinite allowed to interprete the 7 Å peak as only of chlorite. The smectite contents are always very small. Illite and mixed layers illite-smectite (illite layers predominate) are considered as a whole. The other minerals, clinoptilolithe, apatite, analcite, laumontite have appeared sporadically and did not present special identification problems.

For X-raying the grain size fraction of < 2 µm, sample preparation consisted of disaggregating the sample with oxigenated water and ultrasonic bath. Due to the hardness of the rocks, it has not always been possible to get enough material. The carbonatic samples have been treated with monochloric acid. In all the samples the fraction < 2 µm has been separated by means of Atterberg cylinders following Stokes law from a suspension with Na-pyrophosphate as dispergant. Orientated glass slides (air dried, glycolated and heated to 500° C for one hour) have been x-rayed with cobalt radiation. Some samples have been boiled in hydrochloric acid for one hour to dissolve the chlorite, in order to check the presence of kaolinite.

Chlorite and kaolinite were determined according to the method proposed by BISCAY (1964). In the few samples containing kaolinite the peak of 3.60 Å was well resolved by slow scanning from the chlorite and illite peaks (in the range of 3.54 - 3.55 Å). Also in the 7 Å peak the kaolinite contribution could be noted (peak asymmetry towards the low angles). After heating the kaolinite peaks disappeared and the (001) of chlorite became weaker. After boiling in HCl for one hour the chlorite peaks disappeared, but around 3.55 Å there was still a peak due to illite. None or only very small kaolinite peaks were recorded, with the exception of only a few samples.

A random interstratified clay mineral (illite-smectite) is present in most of the samples. In the orientated air dried sample a wide peak around 10.40 Å is observed, which includes the illite peak (10 Å). It shows an asymmetry towards the low angle side (11.40 Å). The residual 10 Å reflection decreases in intensity after glycolation, becoming narrower and symmetric, with a „shoulder“ towards the low angle side (12.80 Å). Normally glycolation produces a raising background from 14 Å, at lower angles sometimes resolved in two peaks (aproximately 17 Å and 34 Å). Besides that, a small peak can occur around 9.50 Å. A lowering of the background on the low angle side (< 6 Å) has rarely been observed. This interlayer component resembles the degraded illites of THOREZ (1976, pp. 50) and it is comparable to the I+10-(10-14) series of the cited author (fig. 35, pp.59).

Weighted peak-area percentages have been calculated for the < 2 µm fraction assuming that illite, chlorite, smectite, mixed layers and kaolinite constitute 100 % of this fraction (Fig. 3). The peak weighting factors used were: (1) the area of the 17 Å glycolated peak for smectite (even when this peak may be originated from the interlayers; see REYNOLDS & HOWER 1970), (2) the difference between the area of the 10.40 Å (orientated sample) and the 10 Å peak (glycolated sample) for the interlayers, (3) four times the 10 Å peak area (glycolated) for illite, (4) twice the 7 Å peak area (chlorite or kaolinite), following WEAVER (1958) and BISCAY (1965).

4. PETROGRAPHICAL AND CHEMICAL CHARACTERIZATION

Three main mudstone types have been recognized: (1) The „radiolaria rich“ mudstones, which contain more than 10 % radiolarian skeletons by volume; (2) the „epiclastic“ mudstones, which have less than 10 % or are barren of radiolarians. They usually show no pyroclastic features, even though they could contain some pyroclastic components and might have been originated from volcanic-pyroclastic material; (3) the „mixed“ mudstones, which are formed by a mixture of tuffs and radiolaria rich mudstones.

4.1 *Longing Sequence*

The Longing Sequence, about 400 m thick, is considered the „type sequence“ for the Ameghino Formation. The radiolarian mudstones and the interbedded tuffs are characteristic features of the sequence. As a consequence a more detailed mineralogical and chemical description of the radiolarian mudstones is presented. It is taken as a reference for the comparison to other sections.

Tab. 1: Mineralogical composition and chemical analyses of major and trace elements of Ameghino Formation rocks. Relative stratigraphic position between localities roughly follows the age (younger to top). Mineralogical composition as determined by X-ray diffraction on bulk sample. Abundance in first order aproximation is the function of peak height for each mineral: ■ = abundant, O = moderate, + = scarce, - = not registered, ? = doubtful determination. QZ = quartz, PL = plagioclase, FK = alkaline feldspar, PY = pyrite, CA = calcite, SM = smectite, IL = illite, CL = chlorite, An = analcite, Ap = apatite, Cli = Clinoptilolite, Ka = kaolinite. Lithologic references: Ō = „epiclastic" mudstone, O = mixed tuffaceous and radiolarian-rich mudstones, X = radiolarian mudstone, V = mudstone with carbonatic concretions.

Sample	CU	PL	FK	PI	CA	SM	IL	CL	Other	Lit.	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	S	Rb	Sr	Zn	Zr
SOB-C																									
SOBC3B	0	0	0	-	+	+	■	■		Ō	61.00	16.06	5.70	0.05	1.60	1.55	1.56	2.79	1.01	0.12	1990	148	131	179	157
SOBC2	0	+	0	-	?	-	■	■		Ō	67.69	17.70	6.30	0.06	2.00	0.73	2.57	3.02	0.75	0.18	789	154	110	119	152
SOBC1	0	+	0	-	?	-	■	■		Ō	65.68	18.42	6.76	0.07	2.25	0.75	1.51	3.17	0.79	0.18	753	156	143	127	153
UPPER SOB																									
SOB66	0	+	+	-	-	-	■	■		Ō	64.85	17.05	6.74		1.89	0.29		4.41	0.74			209	127		
SOB65	0	0	+	-	-	-	■	■		Ō	64.15	13.91	9.26		1.70	1.01		3.18	0.73			130	153		
SOB64	0	0	+	-	-	-	■	■		Ō	65.45	16.15	7.50		1.81	0.25		3.99	0.83			169	121		
SOB63	0	+	+	-	-	-	■	■		Ō	66.23	14.44	7.32		1.80	0.97		3.20	0.71			146	137		
SOB62	0	+	+	-	-	-	■	■		Ō	64.29	14.10	8.48		1.79	0.72		3.24	0.76			143	146		
SOB61	0	0	+	-	-	-	■	■		Ō	63.30	15.99	7.15		1.71	0.39		4.05	0.88			174	142		
SOB60	0	+	+	-	-	-	■	■		Ō	64.72	14.11	8.24		1.88	0.71		3.20	0.77			146	140		
SOB59	■	0	+	-	-	-	■	■		Ō	66.05	14.64	7.12		1.89	1.03		3.19	0.78			157	159		
SOB58	0	0	+	-	-	-	■	■		Ō	63.82	15.04	6.75		1.84	0.84		3.75	0.85			175	158		
SOB57	0	0	-	-	-	-	■	■		Ō	64.07	15.29	7.25		1.79	1.35		3.48	0.84			146	187		
SOB56	0	0	+	-	-	-	■	■		Ō	63.40	14.69	9.15		1.62	2.12		3.20	0.87			131	160		
SOB55	0	+	+	-	-	-	■	■		Ō	64.55	15.76	7.61		1.67	0.96		3.45	0.88			152	164		
SOB53	0	+	+	-	-	-	■	■		Ō	64.63	14.75	8.70		2.08	0.83		3.12	0.87			148	150		
SOB52	0	+	+	-	-	-	■	■		Ō	62.41	15.29	8.66		1.73	1.95		3.48	0.85			157	158		
SOB51	0	+	+	-	-	-	■	■		Ō	66.19	14.19	7.62		1.67	0.85		3.50	0.87			151	143		
SOB50	0	+	+	-	-	-	■	■		Ō	62.77	15.01	8.71		1.67	0.78		3.79	1.00			176	151		
TA																									
TAIII2	0	0	0	■	+	?	■	■		Ō	66.56	15.22	5.74	0.06	1.93	1.25	1.86	2.70	0.65	0.12	9747	143	136	138	139
TAII1	0	0	+	0	+	+	■	■		Ō	65.72	14.36	4.60	0.05	1.44	1.64	2.95	2.20	0.58	0.15	6592	122	330	158	167
TAII	■	+	0	+	-	+	■	■		Ō	65.62	14.25	5.75	0.03	1.47	0.53	2.01	2.77	0.64	0.25	2002	137	148	55	144
TAI2	0	0	0	-	-	?	■	0	An	Ō	64.70	15.95	5.48	0.04	1.37	0.95	2.27	2.42	0.81	0.20	2157	126	276	45	159
MIDDLE SOB																									
SOB45	0	0	0	0	+	?	+	0	An	0	67.61	12.44	4.56	0.05	1.26	0.73	3.04	2.14	0.51	0.30	5531	106	223	116	146
SOB44	■	0	■	+	+	?	+	+		X	73.59	9.34	3.71	0.09	1.05	2.62	2.71	1.27	0.58	0.06	1685	88	185	105	135
SOB43	■	+	0	+	-	-	+	0		X	71.18	9.08	3.86	0.06	0.72	0.33	1.21	2.77	0.41	0.11	3421	127	79	87	127
SOB42A	■	+	+	-	-	?	0	0	Cli,An	X	71.68	6.90	2.99	0.05	0.96	0.51	1.39	1.97	0.45	0.15	471	118	77	74	131
SOB41	■	0	+	0	+	?	+	+	An	X	70.28	9.07	3.15	0.05	0.48	3.06	1.94	2.18	0.46	0.23	8518	97	209	163	139
SOB40	■	■	0	0	+	+	+	+		X	71.93	10.50	3.01	0.06	0.68	1.85	3.93	1.51	0.40	0.10	4770	85	268	117	146
SOB39	0	0	0	■	-	+	0	0	An	0	69.48	11.78	4.44	0.06	1.17	0.84	2.77	2.05	0.50	0.10	12922	99	260	154	147
SOB38	0	■	0	0	-	+	+	■		0	65.58	12.27	5.12	0.06	1.68	0.52	4.09	0.69	0.79	0.13	7151	65	252	175	149
SOB36	■	+	+	-	-	+	■	0	Cli	Ō	76.51	12.33	3.48	0.04	1.15	0.52	1.60	2.37	0.56	0.08	109	121	324	125	142
SOB34	■	+	+	0	-	-	0	■		Ō	75.09	8.42	5.83	0.07	1.89	0.86	1.13	1.15	0.37	0.44	2501	94	65	55	125
SOB33	0	0	+	+	-	+	0	■		Ō	72.04	13.64	5.21	0.05	2.02	0.69	1.44	1.95	0.62	0.10	2206	108	202	97	155
SOB29	■	+	+	-	-	-	0	■		Ō	69.67	11.22	6.95	0.05	1.77	0.57	1.44	1.60	0.51	0.17	296	105	74	88	136
SOB275	0	+	+	-	-	+	0	■		Ō	64.73	9.82	9.29	0.07	2.00	2.29	1.19	0.93	0.38	1.20	558	86	106	69	129

Sample	CU	PL	FK	PI	CA	SM	IL	CL	Other	Lit.	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	S	Rb	Sr	Zn	Zr
LOWER SOB																									
SOB28	■	+	O	-	-	+	■	■		Ö	74.29	13.10	5.20	0.06	1.41	0.48	1.39	2.66	0.47	0.10	663	146	66	89	136
SOB26	■	+	+	-	-	-	O	■		Ö	73.44	9.93	4.76	0.08	1.32	0.68	0.76	1.94	0.39	0.08	545	134	49	90	131
SOB25	O	+	O	O	+	?	+	■		X	61.55	10.75	7.15	0.28	1.92	4.77	1.99	1.42	0.38	0.14	2388	87	181	250	139
SOB24	O	■	+	+	-	+	+	■	Ka	X	66.21	11.44	6.86	0.17	1.37	0.41	3.19	0.83	0.39	0.09	3323	73	175	174	140
SOB23	O	O	O	■	-	-	+	O		X	68.62	8.68	6.98	0.07	0.68	0.25	2.55	1.27	0.51	0.24	7393	82	103	84	129
SOB21	■	O	O	-	+	?	+	+	An	X	77.60	8.86	2.20	0.08	0.45	0.29	3.32	1.56	0.25	0.05	211	91	154	138	135
SOB20	O	■	■	O	-	?	-	O		O	75.05	12.91	4.24	0.09	0.97	0.37	3.22	2.30	0.35	0.08	1461	113	119	75	134
SOB19	O	O	■	■	-	?	+	■		Ö	57.51	13.85	9.58	0.18	2.71	0.64	2.32	2.92	0.85	0.13	7614	105	47	154	156
SOB17	■	O	O	O	-	?	+	■		X	70.90	9.07	5.90	0.10	1.77	0.39	2.50	1.27	0.30	0.20	5560	76	100	151	131
SOB16	O	■	O	■	-	-	+	■		Ö	60.24	13.26	8.03	0.12	2.40	1.08	3.79	1.56	0.81	0.22	13698	82	105	130	130
SOB15	O	■	O	O	-	?	-	O		Ö	68.86	10.27	4.84	0.07	1.52	0.71	4.04	0.89	0.46	0.19	7354	65	171	154	137
SOB11	O	■	■	■	-	?	-	O		O	63.94	11.61	6.04	0.11	1.88	1.22	3.08	1.75	0.71	0.10	13586	82	176	177	127
SOB10	■	■	O	O	-	+	+	+		X	77.86	9.38	3.42	0.05	0.87	1.15	3.55	0.98	0.34	0.09	5179	74	195	129	140
SOB05	■	+	O	-	-	?	O	+		X	74.95	8.09	4.27	0.04	1.14	0.58	0.71	2.01	0.39	0.22	1753	107	80	75	127
SOB04	■	+	O	+	+	-	+	O		X	69.89	9.22	3.71	0.08	1.40	3.91	1.46	1.66	0.37	0.29	2193	102	187	464	135
SOB03	■	O	+	-	-	+	+	+		X	75.41	9.89	3.45	0.03	1.11	0.50	1.77	1.42	0.38	0.05	837	94	226	189	140
SOB02	■	+	+	-	-	+	+	O		X	73.81	8.98	4.66	0.06	1.76	1.49	1.51	1.45	0.30	0.31	3063	90	103	112	122
SOB01	O	■	O	O	+	?	+	O	Cli	O	71.05	11.39	3.47	0.07	1.84	1.91	3.49	1.17	0.36	0.06	479	155	266	227	144
LONGING GAP																									
FA29	■	■	O	■	-	?	+	+		X	77.11	6.57	3.46	0.05	0.45	0.55	3.00	0.73	0.44	0.05	11566	69	58	111	116
FA26	■	+	■	O	-	-	+	-		X	78.16	7.57	2.08	0.03	0.18	0.87	1.29	3.09	0.30	0.10	7343	120	106	140	120
FA23	■	+	+	■	-	-	+	+		X	78.08	5.18	4.12	0.04	0.85	0.71	1.34	0.87	0.32	0.08	11489	74	77	141	117
FA20	■	+	O	O	-	-	-	+	Cli,La,An	X	76.45	6.14	2.81	0.04	0.43	0.64	1.89	1.56	0.33	0.05	8305	86	95	113	123
FA13	■	+	O	O	-	+	+	+		X	78.65	6.58	3.41	0.04	0.58	0.73	1.37	1.98	0.20	0.35	6820	95	43	110	116
FA11	O	O	■	O	-	?	-	+		O	71.00	9.95	3.99	0.06	0.57	1.40	2.21	3.01	0.57	0.08	11748	100	97	104	117
FA6	■	+	O	O	-	-	+	■	Cli	O	70.29	8.01	5.88	0.10	2.00	0.92	0.89	1.75	0.21	0.07	9212	87	710	192	176
FA4B	■	O	■	O	-	-	+	+		X	71.02	8.06	3.47	0.05	0.65	0.92	2.36	2.15	0.43	0.16	11054	87	57	190	122
FA1	O	■	■	■	+	■	+	+	Ka,An	X	68.01	10.30	4.42	0.05	1.58	1.18	3.50	2.06	0.32	0.06	17953	86	99	168	128
GLIDE BLOCK, MOUNT FLORA																									
GD1	■	+	+	-	-	■	O	O		X	74.78	6.25	5.81	0.02	0.89	0.27	0.60	1.36	0.39	0.22	1734	90	3	150	113
MF1	O	+	■	-	-	-	■	■		Ö	61.01	21.38	4.77	0.05	1.31	0.10	1.21	5.04	0.76	0.06	598	236	72	58	151
CARBONATITES (CONCRETIONES IN MUDSTONES)																									
FA12	+	+	+	+	■	-	+	+	Cli	V	9.54	2.27	2.24	2.74	0.88	34.75	0.48	0.31	0.20	0.45	3605	56	137	29	114
SOB6	+	+	+	-	■	+	+	+	Cli	V	17.67	2.78	2.24	0.78	1.05	35.15	0.58	0.36	0.13	0.07	7966	57	115	34	110
SOB7	+	+	+	-	■	+	+	+	Cli	V	32.75	6.01	2.21	0.90	1.12	31.66	1.52	0.94	0.23	0.10	2341	70	141	273	118
SOB9	+	+	+	-	■	+	+	+		V	16.71	2.27	1.53	0.47	0.79	34.57	0.37	0.19	0.11	0.07	3161	58	115	449	112
SOB27	O	+	+	-	O	+	O	■		V	57.47	7.56	8.82	0.43	1.35	12.90	1.72	0.30	0.39	0.18	754	52	119	72	132
TAI1	+	O	+	O	O	+	O	■	An	V	59.29	16.63	6.72	0.07	1.40	6.75	4.21	0.72	0.88	0.19	6187	68	539	109	181
TAII2	+	+	+	-	■	+	O	+		V	16.75	5.04	4.42	0.48	2.04	34.49	0.55	0.55	0.27	0.32	4664	65	336	19	136
TAMITE	+	+	+	-	■	+	O	+		V	14.94	4.52	2.76	0.57	1.40	34.86	1.44	0.55	0.21	0.37	3674	66	347	65	134
TAIII1	+	+	+	+	■	+	O	O		V	28.13	8.07	6.61	0.90	1.39	30.61	1.83	0.76	0.56	0.21	6131	68	152	40	125
TAIII4	+	+	+	-	■	+	■	■		V	30.95	11.56	10.60	1.28	2.57	25.50	1.55	0.85	1.26	0.68	2082	68	181	67	128

Tab. 1: Mineralogische Zusammensetzung und chemische Analyse der Haupt- und Spurenelemente in Gesteinen der Ameghino Formation. Die relative stratigraphische Position der Aufschlüsse folgt etwa dem Alter (höher entspricht jünger). Die mineralogische Phasenzusammensetzung wurde durch Röntgendiffraktometrie der Gesamtproben bestimmt: ■ = häufig, O = weniger häufig, + = selten, - = nicht nachweisbar, ? = nicht eindeutig. QZ = Quarz, PL = Plagioklas, FK = Kalifeldspat, PY = Pyrit, CA = Kalzit, SM = Smektit, IL = Illit, CL = Chorit, An = Analcim, Ap = Apatit, Cli = Clinoptilolith, Ka = Kaolinit. Lithologische Zuordnung: Ö = „epiklastische" Tonsteine, O = Wechsellagerung radiolarienreicher Tonstein und Tuffen. X = radiolarienreiche Tonsteine, V = Tonsteine mit Karbonatkonkretionen.

Because no mineralogical nor geochemical differences have been found between the mudstones of the upper and lower part of the sequence in this locality, the Longing and Ameghino Members of WHITHAM & DOYLE (1989) are described together.

The radiolaria-rich mudstones are structureless or finely laminated. The thickness of the beds range from 0.05 to 20 cm but beds of 0.5-2 cm predominate. Contacts are normally well defined and sharp. Sometimes bioturbation and, more frequently, load structures tend to mix the mudstones with the overlaying tuffs (FARQUHARSON 1983a, WHITHAM & DOYLE 1989). Blue gray to black diagenetic limestones, occasionally form discontinuous horizons 10-20 cm in thickness.

The radiolaria make up some 20 to 70 % of the mudstones showing circular to enlongate sections, the latter always orientated parallel to the bedding planes. The radiolaria skeletons occur as globular mosaics of mainly quartz crystals, sometimes intergrown with plagioclase, pyrite, chlorite and ?titanite crystals. The circular sections are 0.11-0.17 mm in diameter. The long axis of the elongate radiolaria is between 0.19-0.40 mm. They sometimes show increasing size towards the top of the layer. The brownish matrix in which the radiolaria are embedded contains clay minerals, abundant organic matter, pyrite in small grains, quartz, feldspar and a mineral not definitely determined (?epidote) showing high birefringence and high relief. Semi-opaque material is also common. The mudstone laminae may contain up to 10 % of disseminated out of size crystals of quartz and feldspar and very rarely fragments and shards of pumice.

X-ray diffraction analyses (Tab. 1) reveal the relative abundance of quartz, pyrite and alcaline feldspar. There is little plagioclase, illite, chlorite and smectite. Illite-smectite interlayers (10.36 Å) appear only in the clay fraction of the samples from carbonate concretions (FA-12).

The high silica contents are related to the abundance of radiolarian tests, mostly replaced by quartz. Rarely, extensive replacement of radiolarian tests by carbonate and chlorite is visible, like in samples FA-12 and FA-1, in which the silica values are lower (Tab. 1). Alumina is concentrated in feldspar. Sodium and potassium are clearly related to the abundance of plagioclase and alcaline feldspar, indicating that the low amounts of clay minerals are not only relative to the rest of the samples but as well of an absolute meaning. Probably the feldspar content is not only detritic but also authigenic. It appears together with quartz as replacement of radiolarian tests. Among the trace elements the sulphur content (present as pyrite) is remarkably high.

4.2 *Lower Sobral Section*

This part of the sequence is 180 m in thickness and lithologically comparable to the Longing sequence showing an alternation of tuffs and mudstones. The former are thicker and more frequent towards the top (SCASSO & DEL VALLE 1989) meanwhile the mudstones predominate in the lower part of the section. However, the „epiclastic" mudstone levels are thicker and more common than in the Longing sequence.

4.2.1 Radiolarian mudstone

The radiolarian mudstone shows the same range (10-70 %) but in average a lower radiolarian content as in the Longing sequence. There are also more oversized clastic fragments in the brownish mudstone matrix and fragments of pumice occur. X-ray diffraction analysis shows similar contents of quartz and plagioclase, but no alcaline feldspar and pyrite is present. Clay minerals are rare, but on an average more frequent than in Longing rocks. Particularly chlorite is present in increasing amounts. Interlayers (I-M) are detected in sample SOB-3. Kaolinite and analcite appear only sporadically.

The carbonate replacement in samples SOB-6, -7-1, -7-2, -9 and -27 is calcite, other minerals are strongly decreased and pyrite is absent. Clinoptilolite is present in three samples and interlayers I-M (11.15 Å, 10.36 Å, 9.50 Å) are well developed. The carbonatic samples show decreasing amounts of most of the elements with the exception of manganese (higher), strontium, zinc and phosphorus (normal).

4.2.2 Tuffaceous mudstone

These rocks are radiolarian mudstones mixed with tuffs, which therefore have an intermediate composition. An increase of feldspar and decrease of quartz and pyrite is observed. Accordingly, these mudstones have higher alumina and sodium contents, meanwhile silica and sulphur are lowered. Iron and magnesium content is relatively high in agreement with an increasing amount of chlorite.

4.2.3 „E p i c l a s t i c" m u d s t o n e s

These rocks are mudstones and siltstones, massive or parallel laminated, sometimes showing low scale crossbedding. In thin sections a homogeneous rock with a fine-grained matrix (< 0.045 mm) of opaque material, ?feldspar, quartz, chlorite and illite (?sericite) is observed. Some isolated clasts reach about 0.07 mm in diameter. Evidence of slight recrystallization is provided in samples SOB-15 and -26.

X-ray diffraction analysis shows moderate contents of quartz, variable contents of feldspar, increasing amount of pyrite and chlorite, smectite and illite are rare. Samples SOB-26 and -28 represent incipient weathering and silification resultant in the abundance of quartz and the absence of pyrite. In both samples mixed layers (I-S 10.36 Å) have been detected.

From the geochemical point of view these mudstones are, in relation to the radiolarian mudstones, higher in alumina, iron, magnesium, titanium and manganese contents and slightly higher in calcium. The former three elements are involved in chlorite formation, the iron together with sulphur form the pyrite. The others are not clearly correlated with the main minerals but titanium contents are often higher in the tuffaceous mudstones. There is less silica with the exception of samples SOB-26 and -28.

4.3 *Middle Sobral Section*

4.3.1. „E p i c l a s t i c" m u d s t o n e s

These mudstones and siltstones form the lower part of this section which is aproximately 100 m in thickness. The beds are about 4 cm in thickness and interbedded with thick beds (up to 3 m) of volcaniclastic sandstones and tuffs (SCASSO & DEL VALLE 1989). Parallel laminations as well as massive bedding structures are fairly common.

Under the microscope the rocks are homogeneous or show parallel lamination. Small quartz veins with zeolites, feldspar or opaques are frequent as well as semi-opaque seams which are parallel to the bedding planes. Radiolarian tests are scarce but generally present and similar to those of the radiolarian mudstones. Some samples show slight evidence of quartz recrystallization. In the mineral composition the abundance of illite and chlorite is remarkable as well as the low amounts of feldspar and pyrite (low sulphur content). Smectite is scarce and interlayer clay minerals (I-S 10.36 Å, 11.50 Å) are present only in sample SOB-34.

According to the mineralogy, iron and magnesium show high values (chlorite). The abundance of illite is not reflected in the amount of potassium, which is probably due to the low amounts of alcaline feldspar. Low sodium contents are in good agreement with that. Silica is higher than in the normal pelites and values as high as 76 % result from a silification process.

4.3.2 R a d i o l a r i a n m u d s t o n e s

Radiolarian mudstones, about 50 m in thickness, occur in the higher part of the Middle Sobral section. The rocks are stratified showing 2-3 cm thick beds which are interbedded with tuffs. They are usually crossed by small veins.

Under the microscope they show a radiolarian content of about 10 % uniformly distributed through the characteristic dark brown matrix. They show well defined lamination with parallel semi-opaque seams. Often small quartz-feldspar-pyrite veins cross the stratification and the replacement of the radiolarian skeletons presents a similar composition. In the matrix coarser feldspar and quartz clasts are common.

The general mineral and chemical composition is similar to those of the radiolarian mudstones of the Lower Sobral Section, in spite of a little higher amount of titanium.

4.3.3 T u f f a c e o u s m u d s t o n e s

These rocks represent a mixture of radiolarian mudstones and tuffs, which are interbedded with the radiolarian mudstone. Lower silica and higher alumina contents than in the radiolarian tuffs are evident. Iron, magnesium and sodium are raised. The geochemical composition is in good agreement with lower quartz and higher plagioclase, pyrite and chlorite amounts. Analcite is common and interlayers I-S of 10.36 Å and 11.15 Å have been detected. Titanium has no clear behaviour, although this element has been very sensitive to the tuffaceous contamination in the Longing Section.

4.4 Up*per Sobral Section*

Black and gray, marine slaty mudstones compose up to 99 % of the upper member which in minimum is 50 m in thickness. The beds are stratified from a few millimetres to a few centimetres in thickness and show rarely intercalated sandstone beds. This part of the sequence is tightly folded.

Under the microscope parallel lamination and normal gradation from silt to silty clay are frequent. Angular clasts of quartz, feldspar, muscovite and lithics compose the coarser fraction. Sometimes clasts replaced by carbonate or chlorite have been seen. The fine grained fraction is not as dark as in the radiolarian mudstones. Scattered radiolarian tests are visible in some samples. Semi-opaque material is common. Pyroclastic input is not discarded, though no petrographic evidence is detected.

Mineralogically and chemically these rocks are quite homogeneous showing moderate abundance of quartz, moderate to low amounts of plagioclase and low amounts of alcaline feldspar. Chlorite and illite are abundant and correlate with high alumina, iron, magnesium and potassium contents. Titanium is also abundant, silica shows relatively low values. In the clay-size fraction (< 2 µm) illite predominates (Fig. 3).

4.5 T*res Amigos Nunatak Section*

These outcrops show characteristic interbedding of mudstones and tuffs. The slaty mudstones are black to gray and show very fine parallel lamination. They are folded and sometimes cleavage is developed. Carbonate concretions are common.

Under the microscope parallelly laminated siltstones and mudstones predominate. The silty fraction that reaches up to 40 % of the whole rock volume is composed of mostly angular grains of feldspar, quartz, pyrite and of illite (?sericite). Devitrified shards have occasionally been observed and parallel and oblique semi-opaque seams are frequent.

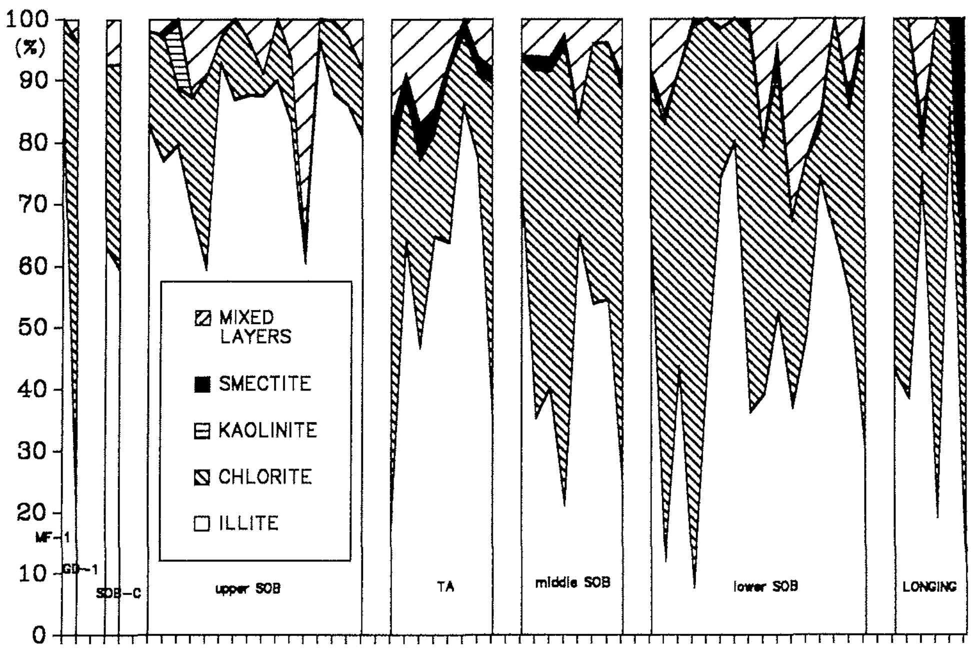

Fig. 3: Clay mineral composition of the clay fraction < 2 µm, recalculated to 100 %.

Abb. 3: Tonmineralzusammensetzung der Feinfraktion < 2 µm bezogen auf 100 %.

X-ray diffraction analysis shows moderate abundance of quartz, plagioclase and alcaline feldspar and abundant chlorite and illite. Interlayers (I-S 10.36 Å) are poorly developed and smectite is scarce. Variable contents of analcite and pyrite are also recorded. In the clay-size fraction (< 2 μm) illite is the more abundant mineral (Fig. 3). According to the abundance of illite high values of potassium and rubidium are recorded. For a smaller extend also magnesium and iron are raised (chlorite). Alumina and titanium are also high, the first in relation to clay abundance, the second probably following the aluminium in diadochal replacement.

Radiolaria mudstones have only been recorded in carbonatic concretions. They comprise up to 15 % of radiolaria replaced by carbonate. In the fine matrix oversized feldspar clasts or pumiceous fragments have been observed. In sample TAII-2 all the minerals occur in small amounts with the exception of calcite and illite. Chemical composition shows lower contents of silica, alumina, titanium, potassium, sodium, rubidium and zinc. Normal contents of iron and sulphur, but high contents of calcium, magnesium, manganese, phosphorus and strontium are recorded.

4.6 *SobC Section*

Stratified beds up to 5 cm in thickness of gray to black tuffaceous rocks, normally graded from very fine-grained sandstones or siltstones to mudstones, were observed. The gradational cycles are about 1-3 cm in thickness. The coarser, very fine-grained sandy to silty part is not thicker than 0.5 cm.

Under the microscope small load structures are clearly visible at the base of the beds. The lower part of each bed is composed of well sorted angular very fine-grained sandstones to siltstones with carbonatic or chloritic cement. Clasts of quartz, feldspar and lithics occur. In some horizons concentrations of vitric shards, replaced by carbonate, have been observed as well as scattered globular skeletons of ?radiolarians. The fine-grained upper part of the beds is muddy and shows grain orientation (quartz, feldspar, chlorite, illite-sericite) parallel to the bedding plane. Mineralogically and chemically these beds show similar features to those of the Upper Sobral section.

4.7 *Glide block sample*

This allochthonous rock represents a hard, grayish-green, parallel laminated mudstone. Unter the microscope it shows 10 % of radiolarian skeletons, elliptical types predominating globular ones. Fine-grained opaques appear in the matrix and semi-opaque material (?iron oxides) is abundant. X-ray diffraction and chemical analyses have revealed abundant quartz, low amounts of feldspar and no pyrite. Moderate contents of illite and chlorite and mixed layers of illite-smectite have been detected. Smectite abundant in the bulk sample has not been found in the clay-sized fraction (< 2 μm). Silica and iron values are remarkable high, but alumina contents are low.

4.8. *Mount Flora Formation*

The sample consists of hard, black, parallelly laminated mudstone showing abundant plant debris on the bedding planes. Under the microscope fine-grained (< 0.045 mm) sericite, quartz and feldspar have been observed. Cleavage is well developed. Illite-sericite is especially abundant. Chlorite and alcaline feldspar are abundant according to very high alumina, potassium and rubidium contents and less high values of iron and magnesium. Pyrite is absent and quartz is moderately abundant. No mixed layers and high crystallinity mica-like clay minerals are characteristic for the clay-size fraction

5. LITHOSTRATIGRAPHIC REMARKS

Some general remarks arise on the basis of the petrographical, chemical and mineralogical studies.

1) A first group of „epiclastic" mudstones (SobC and Upper Sobral sections) without pyrite and with very scarce radiolarian skeletons and abundant clay minerals is defined (Tab. 1). The possible correlation between both outcrops was already pointed out (SCASSO & DEL VALLE 1989) on the basis of the relatively similar stratigraphic position. Epiclastic contribution is proved by the presence of well defined illite-sericite crystals in both sections, which represents a higher crystallinity index inherited from the source rocks, probably a

metamorphic basement. The pyroclastic contribution as thin, graded levels of devitrified shards is clear in the SobC rocks, which are less deformed than the rocks of the Upper Sobral section. In these more deformed rocks devitrified glass shards have not been observed probably due to complete alteration. However, the very similar mineralogical and chemical composition supports a correlation between these two outcrops. These rocks represent the transition between the Ameghino Formation (Upper Jurassic - Berriâsian) and the marine conglomerates (Hauterivian - Barremian) and they are probably of Valanginian age.

2) The second group comprising pyrite bearing mudstones can be divided into two subgroups:
a) a subgroup of dominantly „epiclastic" mudstones with low contents of radiolarians. Such mudstones are present in the Lower Sobral, Middle Sobral and Tres Amigos Nunatak sections showing increasing clastic components with higher stratigraphic position. Abundant chlorite and moderate to abundant illite are recorded.

Titanium and aluminium show higher contents than in the radiolarian mudstones. These elements (as well as Fe and Mg) are normally raised in the mixed pyroclastic-biogenic mudstones (Fig. 4) and therefore suggest a pyroclastic source for these mudstones, although the petrographical pyroclastic features are no longer evident. However, some epiclastic contribution has been determined in the Tres Amigos Nunatak section by the presence of well developed crystals of illite-sericite.

The lower beds of the mudstones of the Middle Sobral section are interbedded with sandstones. They were deposited in a submarine volcaniclastic fan. The presence of radiolarian skeletons, their sedimentary environment and their volcaniclastic origin are feasible with an intercalated position in the Ameghino sequence, though the stratigraphic relations are not clear and different opinions have been given (SCASSO & DEL VALLE 1989, WHITHAM & DOYLE 1989).

b) Radiolaria-rich „biogenic" mudstones represent the second subgroup. They occur in the Longing, Lower Sobral and Middle Sobral sections. The radiolarian content is higher than 10 % by volume and remarkably high amounts of alcaline feldspar occur.

The mudstones of the Longing Section are the most typical and well defined. They contain a higher amount of biogenic material (high quartz and silica contents) and abundant pyrite (high sulphur contents, Fig. 4), but small amounts of clay minerals according to low potassium, magnesium and iron contents. The matrix around the radiolarian skeletons may be composed of devitrified very fine-grained tuffaceous material, as is suggested by geochemical data and isolated shards floating in the matrix.

The glide block sample (GD-1) is also a typical radiolarian mudstone, but the absence of pyrite and the high amounts of iron, not explained by a moderate chlorite content, suggest the presence of iron oxides. Therefore these rocks could not have been deposited in a reducing environment or if so they must have suffered further oxidation during reworking.

From older to younger ages the mudstones tend to have increasing amounts of clastic components and decreasing amounts of biogenic material.. In the Longing sequence, however, the clastic contribution is lower and rather reflects a different paleoenvironmental setting within the basin than a stratigraphic tendency. Following the ages proposed by WHITHAM & DOYLE (1989) the Barremian Tres Amigos Nunatak mudstones show higher clastic contents than the mostly Upper Jurassic Longing, Lower Sobral and Middle Sobral sections but less clastic components than the Upper Sobral and SobC sections of most probably Valanginian age.

6. GENERAL MINERALOGICAL AND GEOCHEMICAL REMARKS

In comparison with the average chemical composition of the pelites presented by SHAW (1956) the samples of the Longing Gap show obviously high contents of silica (ratio of both average values 1.24) and lower amounts of the remaining main elements with the exception of sodium (ratio = 1). Calcium and magnesium values are especially low (ratio 1/3), meanwhile potassium, titanium, aluminium and iron are about 1/2 of the average contents (Fig. 4). On the other hand silica values are lower than in some cherts and related rocks (PETTIJOHN 1957) in which the silica contents exceed 85 % and sometimes reach up to 99 %. A „diatomaceous shale" (HOOTS

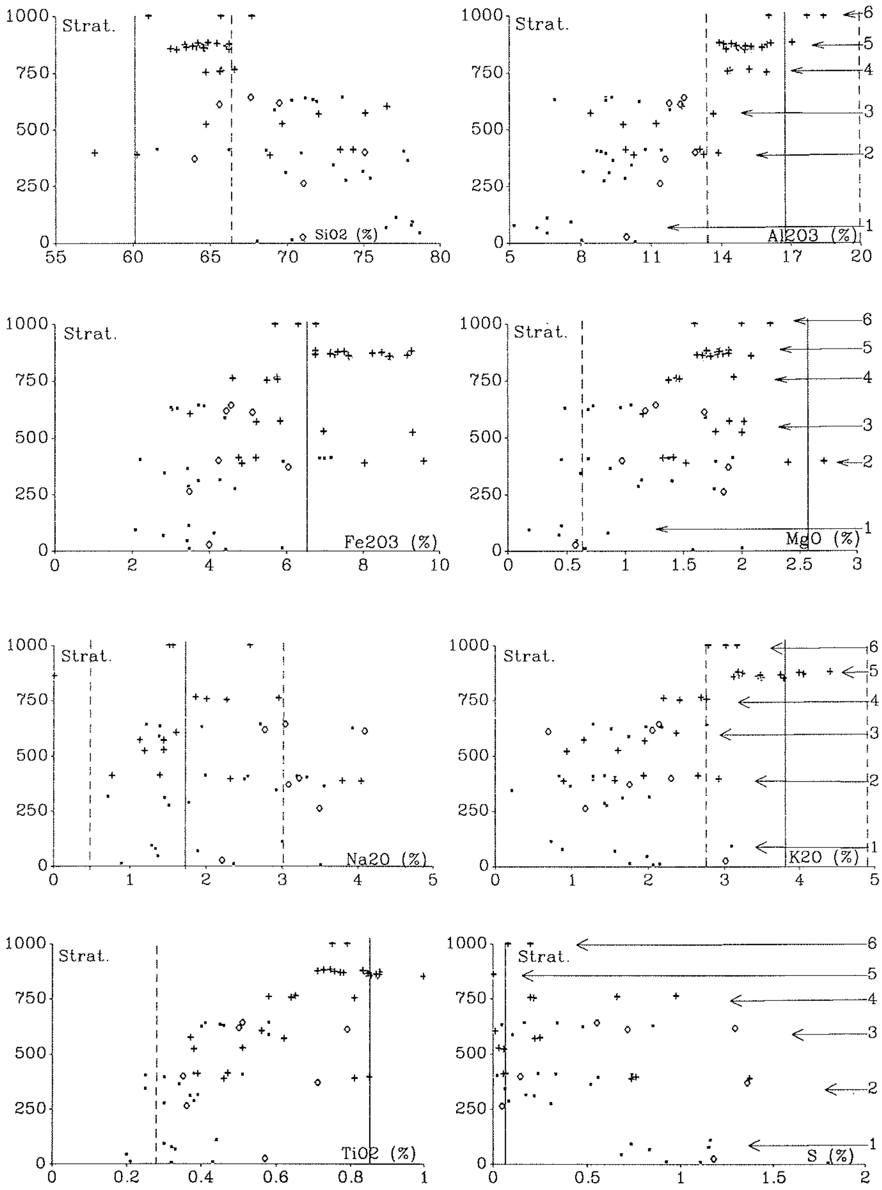

Fig. 4: Weight percentages of SiO_2, Al_2O_3, MgO, Fe_2O_3, TiO2, Na_2O, K_2O and S, showing tendencies for the overall sequence plotted against the stratigraphic position in each locality. Relative stratigraphic position between localities was defined from base to top, roughly following the ages proposed by WHITHAM & DOYLE (1989). 1 = Longing Gap, 2 = Lower Sobral, 3 = Middle Sobral, 4 = Tres Amigos Nunatak, 5 = Upper Sobral, 6 = SobC. Full vertical lines represent the average values for mudstones (SHAW 1954, 1956). Broken lines represent the standard deviation from these values. + = „Epiclastic" mudstones, · = radiolaria-rich mudstones, o = mixed tuffaceous and radiolaria-rich mudstones. Sulphur and sodium have not been measured in Upper Sobral samples.

Abb. 4: Anteile von SiO_2, Al_2O_3, MgO, Fe_2O_3, TiO_2, Na_2O, K_2O und S in Gew.-% des gesamten Bereiches aufgetragen gegen die Stratigraphie. Die relative stratigraphische Lage zwischen den Aufschlüssen folgt in etwa den Altern vorgeschlagen von WHITHAM & DOYLE (1989). Ausgezogene senkrechte Linien geben die durchschnittlichen Werte für Tonsteine nach SHAW (1954, 1956) wieder. Unterbrochene Linien zeigen die Standardabweichung. + = „epiklastische" Tonsteine, · = radiolarienreiche Tonsteine, o = Wechsellagerung von radiolarienreichen Tonsteinen und Tuffen. Schwefel und Natrium wurden in den Upper Sobral-Proben nicht gemessen.

1931 in PETTIJOHN 1957 pp. 364) presents a composition quite similar to those of the Longing beds. The differences are again the very low contents of calcium and magnesium and the high contents of sodium and potassium which occur in the Longing beds. Iron and magnesium show positive correlation (Fig. 5a) and after subtracting the iron content of the pyrite the correlation improves (with the exception of the smectite-rich sample FA-1). Besides the pyrite, the only mineral rich in iron and magnesium is the chlorite. Therefore the Mg/Fe ratio of 0.62 indicates a chlorite of prochlorite type. High amounts of titanium as in sample FA-11 are believed to represent tuffaceous contamination, because the interbedded tuffs show higher titanium contents (SCASSO 1989).

On the other hand the SobC and Upper Sobral sections show marked chemical and mineralogical differences compared to the Longing sequence. In comparison to average values for pelite given by SHAW (1954), they still show high silica contents, but alumina, iron, titanium, potassium, sodium and sulphur are now in normal ranges. Calcium and magnesium are low as well as strontium and zirconium, the latter in comparison to the Littleton Formation beds (SHAW 1954).

The mudstones of the overall sequence are generally rich in silica and poor in calcium and magnesium. Sulphur content is specially high in the lower part of the sequence (Fig. 4) and it is always associated with pyrite abundance. The maxima of sulphur (pyrite) are not related to any lithologic type. High sulphur values also occur in tuff beds. Apparently the main controlling factors were paleoenvironmental conditions, being more reducing near the base of the sequence (i.e. Longing sequence) and changing to more normal values towards the upper part of the sequence.

Positive correlation between titanium and aluminium, magnesium and iron, rubidium and potassium and negative correlation between silica and iron and silica and alumina are observed in the overall sequence (Fig. 5b). These correlations are believed to be due to a common volcanogenic origin for most of the material that forms the Ameghino sequence, because these trends are the normal trends of the andesitic-rhyolitic volcanic rocks, as the interbedded tuffs are (SCASSO 1989). These correlations can not be considered as single dilution effects, because every element is always present in more than one mineral. The mixed tuff-radiolaria mudstone often occupy an intermediate field between the „epiclastic" and the „biogenic" mudstones (Fig. 5b, graphs Si/Al, Ti/Al, Al/K). Moreover, finding the ratio MgO/Fe_2O_3 (total) near 0.3 and the ratio TiO_2/Al_2O_3 around 0.4, there is similarity to the general relation for dacites and trachyandesites (COX et al. 1979, LE MAITRE 1976). Iron-magnesium correlation in modern sediments was discussed by YAMAMOTO (1988) who concludes that strong magnesium-iron correlation is typical for deep sea sediments. Iron rich montmorillonite and olivine are the main mineral phases being residues from halmyrolitic alteration of deep sea basalts. In the case of the Ameghino sediments a deep sea sedimentation is probable but an origin due to basalt alteration can be discarded. YAMAMOTO (1988) noted that by an increase of terrigeneous supply the correlation becomes weaker. This is significant and would mean that in the Ameghino sequence terrigeneous supply was very small. In consequence a general pyroclastic origin can be proposed for most of the material forming the Ameghino sediment sequence.

In the mineral composition of today, chlorite is the main Fe-Mg mineral. These chlorites belong to the iron rich suite as is suggested by the high ratio between the even basal reflections (002/004) in relation to the oddnumbered ones (001/003). According to the table presented by THOREZ (1976) intensities and position of the peaks are typical for prochlorite. This would mean they are formed mainly by alteration of mafics and volcanic glass.

001/002 intensity ratios for illite are between 1.30 and 2.40 in the complete sequence. These values are independant of the stratigraphic position or diagenetic and deformational stage (DUNOYER DE SEGONZAC 1970) and indicate a magnesium rich illite according to THOREZ (1976) criteria. Apparently the chemical composition has no systematic change in the overall sequence even though the illite crystallinity is strongly varied according to the different diagenetic stages. The Al/K correlation graph (Fig. 5b) shows positive correlation for the „epiclastic" and mixed mudstones in which the illite is abundant. The radiolaria-rich mudstones, however, show no correlation in coincidence with the scarce illite content and higher alcaline feldspar content.

7. SEDIMENTARY ENVIRONMENT AND PROVENANCE

Deposition of the Ameghino Formation took place in a quiet anoxic marine basin (FARQUHARSON 1983), where radiolaria-rich mudstone sedimentation was frequently interrupted by ash falls of subaerial volcanic eruptions

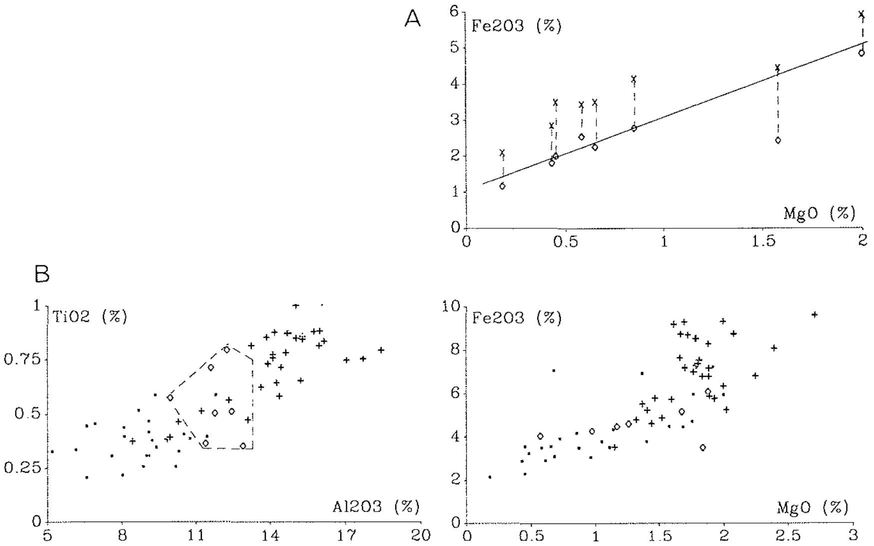

Fig. 5a: MgO-Fe_2O_3 corelation in the Longing Gap radiolaria-rich mudstones. This correlation improves after subtracting the pyrite iron, showing a Mg/Fe ratio of 0.62.

Abb. 5a: MgO-Fe_2O_3-Korrelation der radiolarienreichen Tonsteine von Longing Gap. Zieht man den Fe-Gehalt des Pyrits ab verbessert sich die Korrelation und zeigt dann ein Mg/Fe-Verhältnis von 0,62.

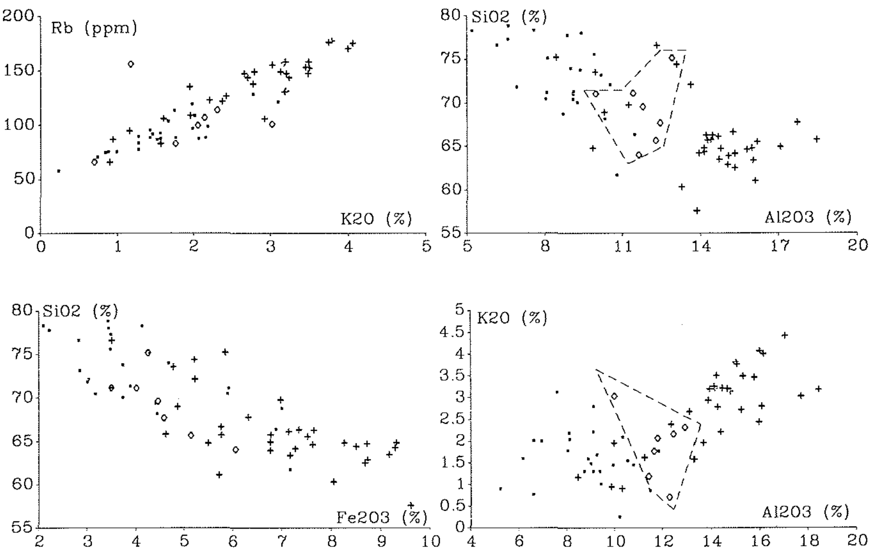

Fig. 5b: TiO_2-Al_2O_3, MgO-Fe_2O_3, K_2O-Rb, Al_2O_3-SiO_2, Fe_2O_3-SiO_2, Al_2O_3-K_2O correlations for the overall Ameghino sequence. + = „epiclastic" mudstones. · = radiolaria-rich mudstones. o = mixed tuffaceous and radiolaria-rich mudstones (encircled).

Abb. 5b: TiO_2-Al_2O_3, MgO-Fe_2O_3, K_2O-Rb, Al_2O_3-SiO_2, Fe_2O_3-SiO_2, Al_2O_3-K_2O Korrelationen für den gesamten Bereich der Ameghino Formation. + = „epiklastische" Tonsteine. · = radiolarienreiche Tonsteine. o = Wechsellagerung von radiolarienreichen Tonsteinen und Tuffen (eingerahmt).

(SCASSO & DEL VALLE 1989). These authors proposed a submarine fan origin for the Middle Sobral and Upper Sobral sections, in which submarine volcaniclastic gravity flows are interbedded with normal tuff and mudstone sedimentation.

The lowest clastic contribution is observed in the Longing mudstone which are richer in biogenic material. The mudstones of the Sobral Peninsula (Lower Sobral, Middle Sobral and Tres Amigros Nunatak sections) show increasing clastic content. It is difficult to decide whether this change is only the result of an overall evolution of the basin with changing general paleoenvironmental conditions (having in this case a stratigraphical meaning), or if it is also the result of a more or less contemporaneous sedimentation in different settings of the basin (Longing and Sobral localities are about 50 km apart). The increasing bioturbation in the Lower Sobral and Middle Sobral sediments and the increasing occurrence of ash beds from gravity flows towards the top of the section as noted by WHITHAM & STOREY (1989) can be the reason for a sediment mixing of pyroclastic and radiolaria rich mudstones, incorporating tuffaceous material into the epipelagic mudstones.

Following the paleontological correlation proposed by WHITHAM & DOYLE (1989) Lower Sobral and Middle Sobral sections are equivalent to the upper part of the Longing sequence. The Tres Amigos Nunatak section, stratigraphically higher in the sequence, presents appreciable quantities of high-crystallinity illite, also indicating epiclastic input into the basin. A general evolution towards less reducing conditions, increasing bioturbation, epiclastic supply and reworking of pyroclastic deposits by sedimentary processes (e.g. gravity flow) and decreasing biogenic sedimentation is suggested.

By the time of deposition of SobC and Upper Sobral sediments the sedimentary conditions were no longer reducing. This points out to the transition of the Barremian conglomerate sedimentation (SCASSO & DEL VALLE 1986, 1989). Even though the bathymetric evolution of the Ameghino Formation is not precisely determined, the presence of radiolaria-rich mudstones implies an hemipelagic sedimentation. The association of volcanic activity and biogenic silica have been known for a long time. RUBEY (1929) proposed that decomposition of fine volcanic ash occurs in the marine water column favouring concurrent precipitation of biogenic silica. KANMERA (1974) indicates that intercalations of tuff and radiolaria chert are common and that the fine-grained matrix around the radiolaria skeletons could be of volcanic origin. Deposits comparable to the Ameghino Formation have been studied by PEDERSEN (1981) in a marine Paleogene diatomite from Denmark. This author relates the diatomite layers to short term anoxic events in the basin.

The original physico-chemical conditions in the Ameghino environment were acid (pH 5-6) and slightly reducing (Eh -0.1 to 0.3) according to the abundance of syngenetic pyrite (GARRELS & CHRIST 1965) and to the good preservation of the siliceous tests. Original Eh and pH conditions favoured the iron solubility (i.e. for small particles of glass and mafics) and reprecipitation as pyrite or mineral neoformation of smectite which is later transformed into illite and chlorite. The clay mineral association with abundant illite and chlorite and without kaolinite is typical for high latitudes (BISCAY 1965, GRIFFIN et al. 1968). However, it is also a typical result of clay diagenesis. Strong evidence for a diagenetic origin of the clay minerals is provided by the abundant presence of illite, interlayers illite-smectite and chlorite in the interbedded tuffs and sandstones, displaying very similar X-ray features like those of the mudstones. Only in Tres Amigos Nunatak, SOB-C and Upper Sobral sections epiclastic illite-sericite has ben recognized. Probably kaolinite was absent from the very beginning of the sedimentation, as should be expected from the mainly volcanic source of the material and from the high paleolatitude. However, kaolinite instability under strong diagenesis precludes any definitive conclusion.

It is not possible to determine exactly up to which extent the clay minerals of the mudstone were originated from suspensions of very fine tuffaceous material. It could have been deposited very slowly after the main tuff event and could have been altered from glass to smectite and then to illite, illite-smectite interlayers and chlorite, up to an extend where they became part of the normal epiclastic sedimentation, being then affected by diagenetic processes. But as already discussed, geochemical relations suggest a calc-alkaline volcanic source for these deposits.

8. DIAGENESIS

The illite, mixed layer (illite-smectite) and chlorite association present in most of the mudstones is a typical diagenetic association. This is strongly supported by the presence of a very similar clay association in the interbedded tuffs and sandstones. For the mudstones an origin due to alteration and devitrification of very fine-grained tuffaceous material is highly possible, as is proved by the positive correlation between some elements (see Fig. 5). Through diagenesis a final association mainly composed of clay minerals, quartz, feldspar and zeolites is developed.

Mineralogical changes in clay minerals with increasing depth were firstly noted by BURST (1959, 1965) who explained the smectite change as due to gradual fixation of potassium and magnesium to form illite and chlorite. Many papers followed this pioneer and, for example DUNOYER DE SEGONZAC (1970) characterized a „late diagenetic domain" by the development of illite and chlorite and the absence of true smectite, among other factors. HOWER et al. (1976) stated that mixed layer clay minerals (illite-smectite) are enriched in potassium and alumina and decrease in silica with depth, apparently due to the reaction

smectite + Al + K = illite + Si

which according to CHAMLEY (1989) can be interpreted as

smectite + K feldspar (mica) = illite + quartz + chlorite

This means chlorite is probably a byproduct of the smectite to illite transformation, utilizing iron and magnesium released from smectite. However, chlorite can also be a direct product of volcanic material alteration as it was observed by HATHAWAY (1979).

The following observations on clay minerals from Ameghino Formation mudstones have some relation to diagenesis:

1) The mudstones show a very homogeneous composition of chlorites and illites.
2) Although the determination of the interlayers is complicated by the presence of illite, chlorite and ?montmorillonite, it is possible to estimate - following the profiles illustrated by REYNOLDS & HOWER (1970) - that not only one but several types of illite-smectite interlayers are present. However, the comparison excluded interlayers with more than 40 % of expandable layers (in the case of illite-smectite random mixed layers) or with more than 20 % of expandable layers (in the case of allevardite-like IM ordered mixed layers).
3) A change in the illite „crystallinity index" and in the wideness of the interlayer-illite peak (10-12 Å) at medium height is observed along the sequence (Tab. 2). The best crystallinity have appeared in the Mount Flora mudstone which is thermally low grade metamorphosed. Upper Sobral, SobC and Tres Amigos Nunatak mudstones show, in relation to mudstones from Longing Gap, Middle Sobral and Lower Sobral sections, better illite crystallinity in both indexes. The only exception comes from the Tres Amigos Nunatak calcareous samples.

	Relative wideness at medium height				C.I.
	10-12 Å		10 Å		
	Range	Average	Range	Average	
Longing Gap	14		13.5		1
Middle Sobral	12-15	(13.75)	9-13	(10.25)	4
Lower Sobral1	2-14	(12.75)	8-10	(9.00)	4
TA calc.	8.5-17	(11.50)	5.5-8	(6.70)	5
TA no calc.	6.5-9.5	(8.00)	7	(7.00)	2
SobC	6.5-10	(8.25)	6.5-7	(6.75)	2
Upper Sobral	4-11	(6.03)	4.5-7	(5.63)	15
MF-1	5		4.5		1

Tab. 2: A change in the illite „crystallinity index and in the wideness of the interlayer-illite peak (10-12 Å) at medium height is observed along the sequence of the Ameghino Formation.

Tab. 2: Über die gesamte Gesteinsabfolge der Ameghino Formation beobachtet man eine Veränderung des Illit-"Kristallinitätsindex", sowie eine Veränderung der Halbwertsbreite des Illit-Wechsellagerungs-Maximums (10-12 Å).

4) Normally the outcropping rocks are fresh and homogeneous. However, in some levels of the Lower Sobral and Middle Sobral sections, silicification or unusual laumontite growth are related to fault planes (e.g. samples SOB-26 and -28).
5) Zeolites (analcite and clinoptilolite) are common products of diagenesis. Both can develop from volcanic glass, though they are not always related to it (KASTNER 1979). Clinoptilolite is also characteristic for sediments of biogenic silica.
6) Carbonatic concretions have probably an early diagenetic origin. Favourable conditions for carbonate precipitation are developed after the first meters of burial, when bacteria induced acid conditions disappear but reducing conditions remain. WITHAM & STOREY (1989) described syndepositional extensional and compressional structures preserved in „early formed carbonatic concretions", developed prior to cleavage in the Tres Amigos Nunatak section.
7) Anastomosing pressure solution seams are common with maximum development in the deformed sections. In the last case also orientated crystal growth is observed. Vertical stylolitic seams are normally observed.

Illite-smectite minerals with 40 to 100 % smectite layers belong to random mixed layers and mostly characterize sediments buried at less than 3.5 km. On the other hand, allevardite-like and superlattice varieties correspond to highly evolved sediments poor in expendable layers and buried deeper than 3 km with temperatures between 100 and 150° C (CHAMLEY 1989). Also higher temperatures (150-200° C) can produce the same effect as strong burial.

X-ray diffractogram comparison between the glycolated samples of the sections with no appreciable epiclastic input (Longing, Lower Sobral, Middle Sobral sections) of the Ameghino Formation and those from wells on the Gulf Coast (PERRY & HOWER 1972) display interesting results. The Ameghino Formation mixed layers are comparable to the mixed layers from 8,379-10,080 feet depth interval (52-37 % expandable layers, well E) and to the 9,504-13,503 feet interval (60-42 % expandable layers, well C).

AOYAGI & KAZAMA (1980) established a mineral zonation for Cretaceous to Tertiary sediments in Japan which is strongly related to overburden pressure, temperature and geological reaction time. These sediments were originally rich in volcanic glass, and the trends registered for the mineral transformations with increasing overburden pressure and temperature were:

1) montmorillonite -> mixed layers -> illite
2) glass -> clinoptilolite -> analcite or heulandite -> laumontite or albite
3) amorphous silica -> cristobalite -> quartz

The association registered in the undeformed to slightly deformed rocks of the Ameghino Formation (quartz, illite, interlayers, analcite, clinoptilolite) presents a clear coincidence with zones E-F and, up to a lesser extend G, of these authors. This corresponds to Cretaceous - Tertiary rocks buried between approximately 2,700-4,000 m and a temperature interval of about 100-150° C.

However, the Longing Gap section and the Lower Sobral and Middle Sobral sections from the Sobral Peninsula have not undergone extreme heating as it is indicated by vitrinite reflectance values of 0.53-0.57 % and 0.51-0.56 % respectively (WHITHAM & STOREY 1989).

According to the mineralogical indicators of the classification by FOSCOLOS et al. (1976) the Longing Gap, Lower Sobral and Middle Sobral sections are in the „late mesodiagenetic stage", characterized by the usual absence of kaolinite and mixed layers (I-S) with 25-50 % of expandable layers. There is no good agreement between vitrinite reflectance values of 0.51-0.57 % presented by WHITHAM & STOREY (1989) and the mineralogical indicators determined here. Higher values of 1.0-1.5 (Ro max.) should be expected for a late mesodiagenetic stage (FOSCOLOS et al. 1976), in better agreement with the Ro values presented by MACDONALD et al. (1988) for the arc terrane samples (from 0.54-4.0 %) of the Ameghino (Nordenskjöld) Formation.

To summarize, the Longing Gap, Lower Sobral and Middle Sobral mudstones indicate a late mesodiagenetic stage (FOSCOLOS et al. 1976). Comparison with other sequences suggest burial depths of 2,500-4,000 m and a temperature range of 100-150° C.

Although the Upper Sobral, SobC and Tres Amigos Nunatak sections have an upper stratigraphic position, they appear to be in a more evolved diagenetic stage considering the illite. Inheritance of mica-illite of higher crystallinity due to epiclastic supply is the only reason for this inconsistency, because a differential thermal history is rather unlikely (the Upper Sobral and SobC outcrops are very close to the outcrops of the Lower Sobral and Middle Sobral sections, see Fig. 1). Moreover, no illite recrystallization has been observed even in the most deformed rocks, and as WEAVER (1989) pointed out, no illite recrystallization occurs without adequate temperature, even through important stress. In consequence, an epiclastic supply from the low grade metamorphic Trinity Peninsula Group of upper Paleozoic to Triassic age is highly probable.

Ameghino Formation rocks show strong lithification and the presence of about 1,000 m of Hauterivian - Barremian conglomerates (which is a minimum thickness since base and top are not exposed) cropping out close to the Ameghino Formation exposures on the Sobral Peninsula, suggest that they have undergone considerable burial and relatively high temperatures (a high geothermal gradient is expected at a location close to a volcanic arc). However, vitrinite reflectance values are not consistent with the diagenetic stage pointed out by the mineral indicators. It is not clear to which extent syndepositional deformation have spanned dewatering, lithification and mineral transformation beyond the normal ranges of the burial overburden pressure and temperature, as is suggested by WHITHAM & STOREY (1989). But it is possible to state that the rocks of the Sobral Peninsula and probably of the Longing Gap have suffered considerable burial and temperature influence.

9. ACKNOWLEGEMENTS

The authors wish to acknowlege the Instituto Antártico Argentino for logistic support of the field trip and the Deutsche Forschungsgemeinschaft for financial support. Lics. del Valle and H. Núnez kindly provided the Longing samples for this study. Many thanks to Klaus Preissinger and to Dr. Wolfgang Köhler for their assistance in the use of computer programs and laboratory work. Part of this work was carried out by means of CONICET (Consejo Nacional de Investigaciones Cientificas y Téchnicas de la República Argentina) fellowship.

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