Temas de la Geología Argentina I (2) INSUGEO, Serie Correlación Geológica, 21:171-196
Tucumán, 2006 - ISSN 1514-4186 - ISSN 1666-9479 en línea

The Lower Ordovician Diablo Formation (nom. nov.) in the southern Puna (NW Argentina): Link between the northern Puna and the Sierra Famatina

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Abstract. *The Lower Ordovician Diablo Formation (nom. nov.) in the southern Puna (NW Argentina): Link between the northern Puna and the Sierra Famatina.* Recently defined volcaniclastic rocks deposited in the southern Puna during the Arenig can represent the link between volcanogenic deposits of the northern Puna (Aguada de la Pérdiz Formation) and the Sierra Famatina (Suri Formation). Finds of *Phyllogratus* sp. points to a deposition during the Arenig. The rocks are defined as Diablo Formation (*nom. nov.*) and comprises seven different lithofacies (volcaniclastic sandstones, volcaniclastic siltstones, volcaniclastic mudstones, volcaniclastic greywackes, silicified rocks, pyroclastic flows, peperites) as well as syndepostional rhyolitic to andesitic volcanites. Petrographic studies reveals a variation in composition between Q_t 17-45 F 17-44 L 25-56 (average Q_t 24 F 30 L 46), L_v/L 0,13-0,48, $Lv_{intermediate}/Lv_{felsic}$ 1:2 and P/F 0,45-0,79. Cathodoluminescence analyses show that nearly 90% of the quartz grains are of volcanic origin. Unequivocal relicts of basaltic volcanism could not be found in the mineralogy. The mainly volcanic source observed in the framework mineralogy coincides with the heavy mineral composition, which includes hornblende and apatite, and several elongated zircons showing gas or melt inclusions. Illite crystallinity measurements show an anchimetamorphic overprint comparable to the Prehnite-Pumpellyite facies. Weathering affected the composition of alkali elements, which reflect the grade of alteration rather than giving provenance information. Trace element geochemistry shows a rhyodacitic to dacitic composition and rare earth element (REE) patterns are slightly depleted in light REE and enriched in heavy REE. Some samples show a positive Eu-anomaly, low Th/Sc ratios (< 1) and depleted concentrations of Nb, Ta and Ti, pointing to a continental arc source. Nd-isotope data reveal model ages (T_{DM}) between 1.1 –1.4 Ga with $e_{Nd(t)}$ of about -1 to -5. This coincides with the data for the synsedimentary volcanic rocks. Mixing models based on Nd-isotopes show the influence of c. 80-90% volcanic material mixed with typical upper crustal material of the region, which coincides with the petrography. The detrital material of the Diablo Formation was derived mainly from southern sources and was deposited in a volcanic apron. It also received material from sedimentary, metamorphic and plutonic sources, which indicates that the tectonic setting was that of a retro-arc basin. The formation is part of the Puna Volcanic Complex and stratigraphically correlated with the Volcanosedimentary Successions in the northern Puna and the Suri Formation of the Sierra Famatina. This implies that the Famatinian arc could have extended northwards into the Puna region.

Resúmen: *La Formación Diablo del Ordovícico Inferior de la Puna Sur (NW Argentina): unión entre la Puna y Sierra de Famatina.* Las recientemente definidas rocas vulcanosedimentarias de la Puna Austral depositadas durante el Arenigiano, representan la conexión entre los depósitos vulcanosedimetarios de la Puna del Norte y la Sierra Famatina. Estas mencionadas sucesiones están definidas como Formación Diablo (*nom.nov.*) y contienen siete diferentes litofacies (areniscas vulcanosedimentarias, limos vulcanosedimentarias, pizarras vulcanosedimentarias, grauwacas vulcanosedimentarias, chert, flujos piroclasticos, peperitas). Las rocas sedimentarias están asociadas con flujos de lavas sin-sedimentarias de la composición riolítica y andesítica. Estudios petrográficos señalan la siguiente composición en las sedimentitas: Q_t 17-45 F 17-44 L 25-56 (promedio Q_t 24 F 30 L 46), L_v/L 0,13-0,48, $Lv_{intermediario}/Lv_{felsico}$ 1:2 y P/F 0,45-0,79. Los análisis de catodoluminescencia comprobaron que casi 90% del cuarzo es de origen volcánico. Ademas de circones, rutilos y turmalinas, los minerales pesados más abundantes son anfíboles y apatitas, que indican una fuente magmática. La cristalinidad de ilitas muestra una facies metamórfica de bajo grado comparable con la facies Prehnite-Pumpellyite. Brachiopodos y graptolitos fueron encontrados en las sucesiones, pero solamente *Phyllograptus* sp. fue posible de identificar e indica una edad Arenigiano hasta Llanvirniano Inferior. Los análisis geoquímicos de los elementos de

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trazas muestran una composición general riodacítica hasta dacítica. Los patrones de tierras raras están empobrecidas en tierras raras livianas, pero enriquecidas en tierras raras pesadas. Sin embargo, varias muestras poseen una anomalía positiva en Eu. Las rocas están caracterizadas con relaciones bajas (<1) en Th/Sc y empobrecimiento en los elementos claves Nb, Ta y Ti, típico por un arco volcánico continental. Análisis geoquímicos de las lavas muestran también un origen como un arco volcánico continental. Isótopos de Nd poseen edades modelos entre 1,1 y 1,4 Ga con ?$_{Nd(t=470Ma)}$ entre -1 y -5. Estas características coinciden con los datos de los isótopos de Nd de las rocas volcánicas en el mismo perfil. Escenarios de mezcla modelados con los isótopos de Nd exigen 80-90% material volcánico mezclado con 10-20% de material de la corteza continental superior expuesto en rocas pre-Ordovícicas de la región. Estos modelos son confirmados por la petrografía.El material detrítico de la Formación Diablo fue transportado desde fuentes australes y depositado en un abanico volcánico en la cuenca retro-arco del arco continental Puna-Famatiniana. La Formación Diablo es parte del complejo volcánico de la Puna y puede ser correlacionada con las sucesiones vulcanosedimentarias de la Puna del Norte y la Formación Suri del Sistema Famatiniano lo cual implica una prolongación del arco Famatiniano hacia el norte a la Puna.

Keywords: Puna, Diablo Formation, Arenig, continental arc deposits, provenance, tectonic setting

Palabras Clave: Puna, Formación Diablo, Arenigiano, Depósitos de arco continental

Introducción

The objective of this contribution is the first detailed description under the name Diablo Formation of the volcanigenic deposits of Ordovician age in the southern Puna of northwestern Argentina (Fig. 1). Different methodological approaches are used (paleontology, sedimentology and petrography, geochemistry including isotopegeochemistry) to define this new formation.

The rocks are exposed in the Quebrada Diablo in the central part of the Sierra Calalaste (Province Catamarca) in the northwest of Argentina, 35 km southwest from Antofagasta de la Sierra (S26º02'46,8''-26º03'37,3''; W67º36'37,8''-67º37'24,1''). J. Guillou (Provincial Mining Secretary, Salta) was the first to note this rock association in unpublished material .He described pillow lavas in the Quebrada Diablo on a schematic map of the Sierra Calalaste. Since 2002, the access has been improved enormously as a new road from Antofagasta de la Sierra to Quiñoas (Salar de Antofalla) was built. Probable equivalents of the formation are exposed 20 km further to the south in the Quebrada Trasmontana, where volcaniclastic rocks and dacites occur (Fig. 1b). Here, only preliminary studies were carried out (Zimmermann and van Staden, 2002). Detailed provenance studies are currently under way.

Next to the definition of the Diablo Formation, the objective of this paper is to characterize the volcano-sedimentary deposits as detailed as possible to enhance the basin models for the Puna and Famatina basin during the Ordovician (e.g. Bahlburg, 1990, 1998; Clemens and Miller, 1996; Zimmermann and Bahlburg, 2003).

Outcrop and Geological Context.

New finds of graptolites and isotope-geochemical age dating improved the stratigraphy of the Lower Ordovician units in the southern Puna (Fig. 2; Zimmermann et al., 1998; Kleine et al., 2004). The oldest Ordovician sedimentary rocks are represented by the Tolar Chico Formation (after Zappettini et al., 1994, redefined in Zimmermann and Bahlburg, 2003). This unfossiliferous formation contains thick quartz arenites as well as thin layers of very-fine grained wackes displaying grading and ripple cross lamination. The presence of thick turbidite packages and the absence of shallow water deposits indicates a marine environment below wave base. The Tolar Chico

Formation is concordantly overlain by the Tolillar Formation (after Zappettini et al., 1994, redefined in Zimmermann and Bahlburg, 2003). At the base it consists of rare medium-grained quartz arenites, which give way to volcaniclastic sandstones, quartz–rich siltstones and shales. Fine- to coarse-grained volcaniclastic greywackes and massive feldspathic greywackes are the most abundant lithologies. Flute marks, ripple cross and parallel lamination indicate deposition from turbidity currents. Debris flow deposits consisting of immature detritus are interbedded with the turbidites as well as shale horizons. The immature material points to only minor reworking between source and sink. The sedimentary sequence shows mylonitic contacts to basic and ultrabasic rocks, and both rock types are intruded by the Complejo Igneo Pocitos (476±2Ma; Kleine et al., 2004). The top of the formation is not exposed. In the central part of the Sierra de Calalaste (Quebrada Diablo, Fig. 1b) the here described volcanogenic unit of Arenig to Lower Llanvirn age crops out. These volcanogenic units contrast markedly with the overlying Coquena and Falda Ciénaga formations exposed to the north and east of the Quebrada Diablo and northern Sierra Calalaste (Zimmermann et al., 2002).

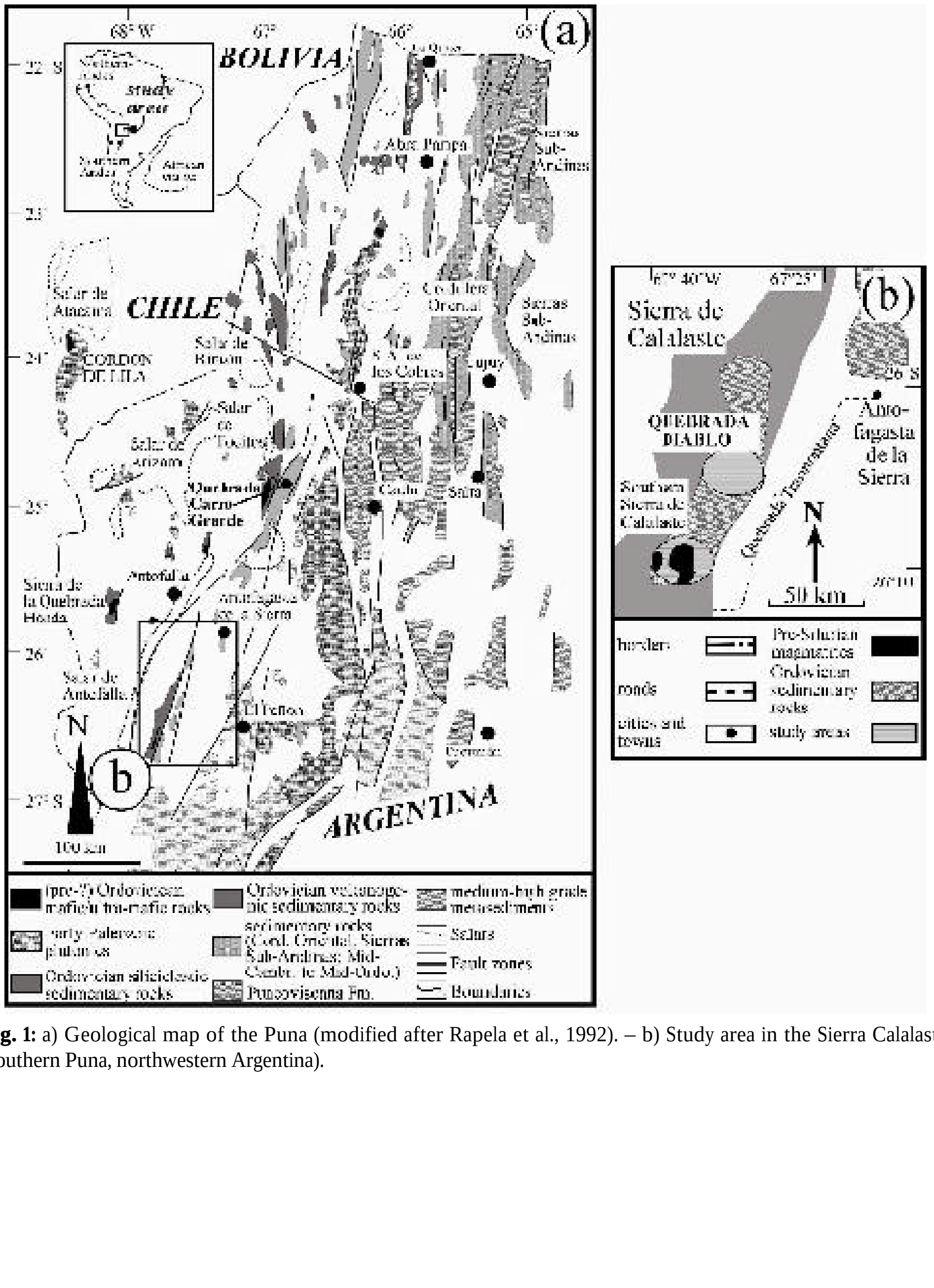


Fig. 1: a) Geological map of the Puna (modified after Rapela et al., 1992). – b) Study area in the Sierra Calalaste (southern Puna, northwestern Argentina).

The entire Ordovician sedimentary successions, including basic to ultrabasic bodies, are isoclinally folded with folds commonly verging westwards. Towards the south, the deformation increases clearly and the vergence becomes more variable. The cleavage is predominantly parallel to the bedding in the coarse units. In pelitic rocks, two cleavages may be developed locally. The grade of metamorphism is determined as very low by illite crystallinity and points to the Prehnite-Pumpellyite facies. This is in accordance to earlier studies on Llanvirnian strata in the southern Puna by Toselli (1982).

The Diablo Formation (*NOM. NOV.*)

Generals

The sedimentary rocks are interlayered with rhyolitic to andesitic lava flows, which show quenched contacts and peperites at their base. The clastic sequences are comprised of conglomeratic to fine-grained rocks. Grain-size variation occurs rapidly. Thus, the formation cannot be differentiated in smaller mapable units or members in its type locality, besides the occurrence of lava flows. Since, the lava flows occur partly massive but as well intercalated the definition of a member seems at this stage not useful. The rocks are mainly isoclinal folded, striking N-S to NNW-SSE and plunge generally to the east with steep angles between 40°-85°. The top of the section lies in the west. The base is not exposed, and the top is covered by Cenozoic volcanic material. Fossil material could only be found at the base of the sequences. The thickness of the section is about 500 m (Fig. 3). Towards the east, in the Quebrada Trasmontana Middle Ordovician rocks of the Falda Ciénaga formation are exposed. The contact is fault-bounded. However, the fault can only be observed by airfotos or satellite images, in the field the contact is buried by regolith.

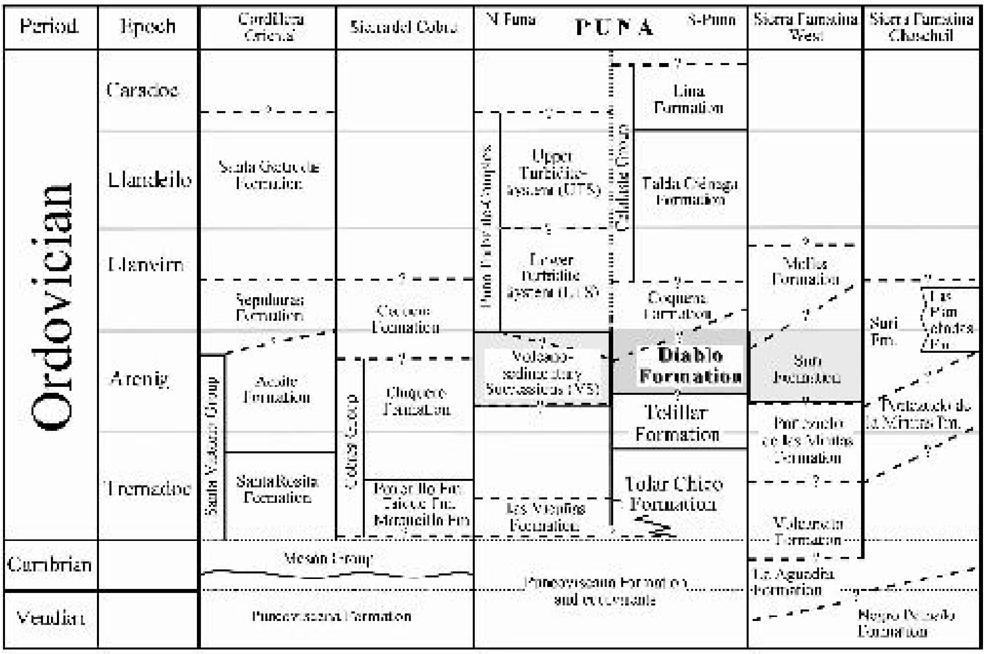


Fig. 2: Stratigraphic table of the Early Paleozoic of NW Argentina. The grey shading marks the stratigraphy discussed in this (compilation of stratigraphic in Aceñolaza and Baldis, 1987, Bahlburg and Hervé, 1997, Zimmermann, et al., 2002).

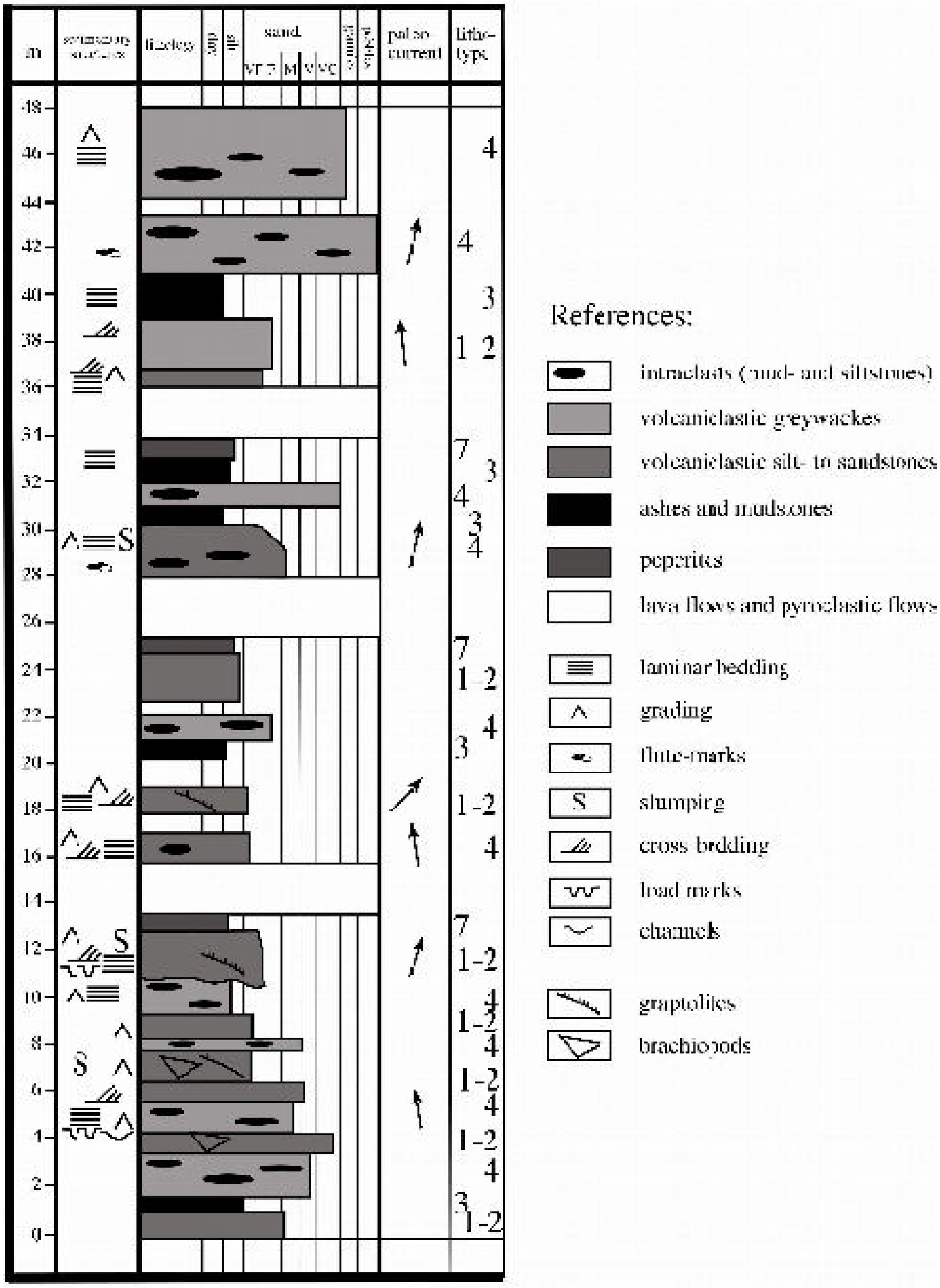


Fig. 3: Condensed lithostratigraphic profile as isoclinal folding causes repetition in the Quebrada Diablo. (VF= very fine; F= fine; M= medium; C= coarse; VC= very coarse sand).

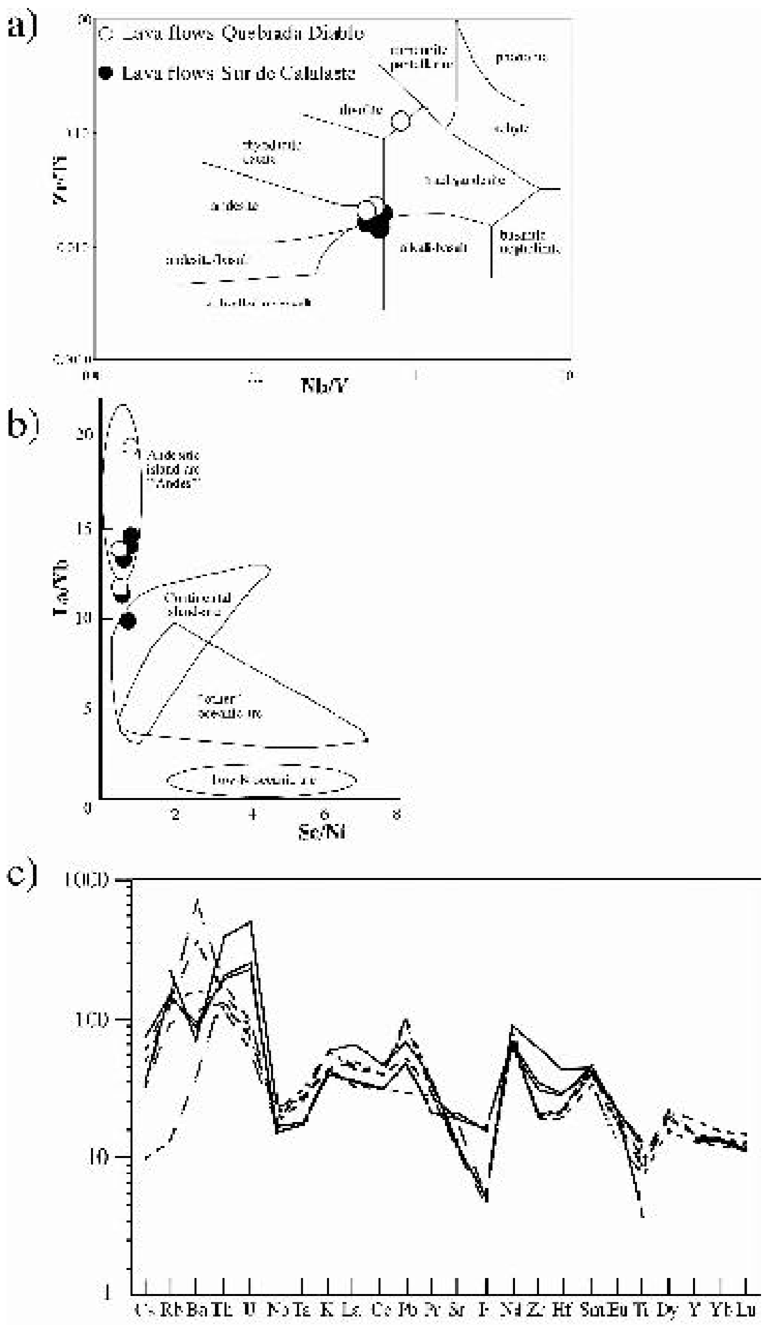


Fig. 4: a) Composition of the volcanic rocks from the Diablo Formation in comparison with dacites from the southern part of the Sierra de Calalaste (after Winchester and Floyd, 1977). The lava flows are mainly andesitic to dacitic in composition besides one sample, which is a rhyolite. - b) Diagram to elaborate a trend for a paleotectonic setting (after Bailey, 1981). It can be seen that La/Yb relations are typical for arc rocks as well as the Sc/Ni ratios, and that both suite show clear similarities. c) Normalisation of trace and selected major elements to chondrite after Sun and McDonough (1989), which shows clearly negative anomalies in Ta, Nb and Ti, and a positive anomaly of Pb, typical for subduction (continental arc) related rocks.

The thicknesses of the intercalated lava flows vary between 5 m and 80 m. However, duplication of the layers is very probable caused by the isoclinal folding. Hyaloclastites or autobrecciated deposits, as well as pillow lavas are not found. “Pseudo-pillow” structure are recognized and produced by weathering. The lava flow in the entrance of the Quebrada (towards the east; Fig. 1b) shows a higher content of quartz, where the flows further to the west, higher in the stratigraphy, are richer in feldspar. Hydrothermal alteration affected the rocks, and chlorite, calcite and albite are the most common phases. Some ghoststructures of amphiboles and plagioclase could be observed. The main porphyroclasts are quartz, showing resorption embayments, and albite as well as plagioclase (anorthite content 15-30%). The crystals are up to 2 cm large and mainly affected by fluid flow, which dissolved partly crystal boundaries. In some samples biotite could be identified. The matrix is mainly formed of quartz, chlorite and albite. Only in two samples trachytic flow textures occur. The geochemistry and isotope geochemistry of the rocks is added to the data of the sedimentary rocks (see Table 3 and 4). The trace element ratios point to a mainly andesitic composition (Fig. 4a) and to a continental arc setting (Fig. 4b). The pattern in a spider diagram (Fig. 4c) normalized to chondrite (after Sun and McDonough, 1989) show a significant depletion in all elements, which discriminates a subduction zone setting with the influence of continental crust. Thus, negative anomalies are given for Ta, Nb, Ti but an enrichment in Pb (according to Hofmann, 1988, 1997). These characteristics point clearly to a continental arc environment.

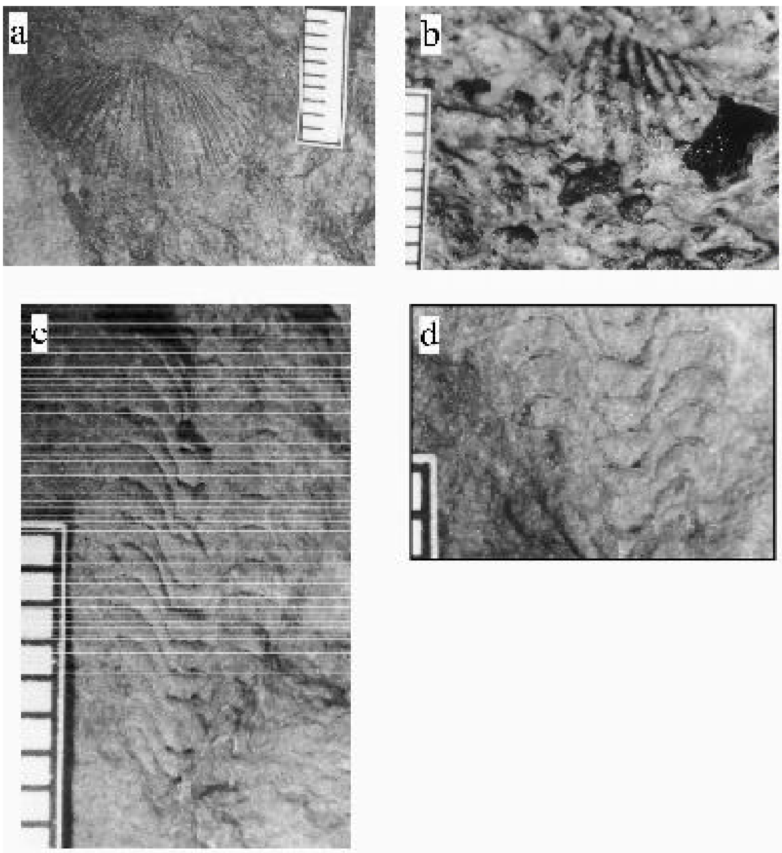


Fig. 5: a) Fine ribbed shell of an orthide from lithotype 2. – b) Coarse ribbed shell of an orthide from lithotype 4. – c) *Phyllograptus* sp. from lithotype 4. – d) Detail of the lower part of a *Phyllograptus* sp. specimen.

Sample	B 10	B 15	B 16	B 27	B 30	B 31'
Rocktype	feldspathic litharenite	lithic arkose	feldspathic litharenite	feldspathic litharenite	lithic arkose	feldspathic litharenite
Grain size (phi)	3 (-0,1)	3 (-2,5)	3 (-0,6)	3	3	3 (-0,1)
Counts	367 (413)	307 (400)	364 (402)	312 (376)	239 (301)	19,97-28,87-51,27
Qt-F-Lt	18,68-28,79-52,53	30,74-43,70-25,56	20,07-29,07-50,87	32,07-31,27-36,21	22,51-17,32-60,17	17,30-29,90-52,80
QmFLt	17,39-29,25-53,36	23,98-47,97-28,05	17,50-30,00-52,50	15,09-39,66-45,26	07,25-20,73-72,02	37,04-28,02-34,94
Qm-P-K	37,29-22,88-39,83	33,33-12,99-53,67	36,84-27,82-35,34	27,56-24,41-48,03	25,93-24,07-50,00	0,4,41-47,92-47,67
Qp-Lv-Ls	37,29-48,31-14,41	35,33-31,74-32,93	34,27-39,86-25,87	27,56-55,91-16,54	25,93-33,33-40,74	36,73-34,69-28,57
Lm-Lv-Ls	11,11-35,56-53,33	01,45-18,84-79,71	03,40-48,30-48,30	14,29-26,67-59,05	02,88-13,67-83,45	03,70-48,15-48,15
Quartz	48	83	58	93	52	64
Quartz monocrystalline (Qm	44	59	49	35	14	54
Quartz polycrystalline (Qp)	4	20	7	55	13	8
Chert	0	4	2	3	25	2
Feldspar (F)	74	118	84	92	40	92
Plagioclase (P)	57	53	57	71	18	51
Alkalifeldspar (K)	17	55	37	21	22	42
Lithoclasts	135	69	147	105	139	162
Lithoclasts sedimentary (Ls)	72	55	71	62	116	78
Lithoclasts metamorphic (Lm	15	1	5	15	4	6
Lithoclasts volcanic (Lv)	48	13	71	28	19	78
Matrix	11,14	23,3	9,45	20,25	20,7	8,4
Lv/L	0,36	0,19	0,48	0,27	0,14	0,45
P/F	0,77	0,45	0,68	0,77	0,45	0,55
Heavy minerals	5	24	18	14	2	19,8
Phyllosilicates	44	2	49	8	1	53,9
Others	53	11	17	0	4	18,7

Sample	B 117	B 119	C 10	C 39	C 43	B 43-2
Rocktype	feldspathic litharenite	lithic arkose	feldspathic litharenite	feldspathic litharenite	lithic arkose	feldspathic litharenite
Grain size (Phi)	1	2,5 (-0)	3 (-0,1)	3 (-0,1)	1	3 ((-2,5))
Counts	313 (356)	303 (404)	431 (509)	509 (598)	403 (474)	284 (365)
Qt-F-L	17,65-32,35-50,00	19,92-24,14-55,94	18,35-29,79-51,86	24,75-35,95-39,53	19,12-24,14-55,84	45,95-23,94-30,12
QmFLt	16,95-32,63-50,42	19,31-24,32-56,37	17,04-28,98-53,98	19,87-38,28-41,84	18,51-24,32-57,12	12,50-38,75-48,75
Qm-P-K	34,19-27,35-38,46	44,25-23,89-31,86	37,32-23,01-39,66	34,17-29,14-36,69	44,05-23,69-32,26	24,39-29,27-46,34
Qp-Lv-Ls	34,19-44,44-21,37	01,35-18,24-80,41	37,59-43,97-18,44	34,12-36,33-29,50	44,22-44,22-11,56	24,39-29,27-46,34
Lm-Lv-Ls	01,68-34,45-63,87	00,00-18,50-81,50	11,11-35,8-53,09	07,50-40,50-52,00	00,00-13,33-86,66	14,10-41,03-44,87
Quartz	42	52	58	126	68	119
Quartz monocrystalline (Qm	40	50	53	95	65	20
Quartz polycrystalline (Qp)	1	2	5	25	3	86
Chert	1	0	0	6	0	13
Feldspar (F)	77	63	89	183	82	62
Plagioclase (P)	52	27	62	101	65	24
Alkalifeldspar (K)	25	36	26	82	17	38
Lithoclasts	119	146	162	200	190	78
Lithoclasts sedimentary (Ls)	76	119	86	104	155	35
Lithoclasts metamorphic (Lm	2	0	18	15	0	11
Lithoclasts volcanic (Lv)	41	27	58	81	35	32
Matrix	10,69	25,2	18,5	21,1	17,5	18,5
Lv/L	0,34	0,18	0,36	0,41	0,18	0,41
P/F	0,68	0,43	0,7	0,55	0,79	0,55
Heavy minerals	2	11	6	26	24	17
Phyllosilicates	10	1	52	2	14	10
Others	63	12	64	12	25	8

Sample	B 58	B 61	Average
Rocktype	feldspathic litharenite	feldspathic litharenite	
Grain size (Phi)	4 (-1)	3 (-1)	
Counts	341 (424)	387 (431)	322 (387)
Qt-F-Lt	32,92-31,28-35,80	22,04-30,92-47,04	26,00-29,00-45,00
QmFLt	32,08-31,67-36,25	17,42-32,75-49,83	17,95-32,77-49,28
Qm-P-K	50,33-09,15-40,52	34,72-17,36-47,92	34,88-21,92-43,20
Qp-Lv-Ls	50,33-22,22-27,45	34,72-38,19-27,08	
Lm-Lv-Ls	11,49-31,03-57,47	00,70-13,29-86,01	06,11-28,13-65,76
Quartz	80	67	28,43
Quartz monocrystalline (Qm	77	50	18,21
Quartz polycrystalline (Qp)	3	17	7,64
Chert	0	0	2,57
Feldspar (F)	76	94	35,71
Plagioclase (P)	34	55	21,93
Alkalifeldspar (K)	42	39	13,86
Lithoclasts	87	143	54,07
Lithoclasts sedimentary (Ls)	50	123	32,43
Lithoclasts metamorphic (Lm	10	1	3,29
Lithoclasts volcanic (Lv)	27	19	18,36
Matrix	20,65	11	6,66
Lv/L	0,31	0,13	0,14
P/F	0,46	0,59	0,69
Heavy minerals	13	11	5,91
Phyllosilicates	42	1	11,28
Others	43	12	7,41

Table 1: Complete point-counting results of the Diablo Formation (counted after Ingersoll et al. (1984), where Qt include polycrystalline quartz, and L only lithoclasts, but Lt lithoclasts, chert as well as polycrystalline quartz.

Sample	Zircon	Tourmaline	Rutile	Monazite	Apatite	Amphibole	Others	Opaques	Sum	ZTR
B 32	48	3	1	1	15	7	2	34	111	68
B 48	143	2	9	2	5	26	0	15	202	82
B 4	16	2	2	0	4	6	2	0	32	63
B 59	100	8	2	0	28	16	16	30	200	65
B 60	35	9	2	2	9	21	9	28	115	53
B 62	37	6	4	1	3	18	2	35	106	66
B 86	74	0	6	3	3	30	3	40	159	67
B 94	54	0	6	0	12	29	6	62	169	56
B 113	45	2	4	1	3	15	1	29	100	72
B 130	143	14	0	1	65	36	0	14	273	59
B 127	23	3	3	3	10	19	1	38	100	47
Sum	718	49	39	14	157	223	42	325	1567	
Average	65	4	4	1	14	20	4	30	155	63

Table 2: Quantification of the heavy mineral assemblage. ZTR value after Hubert (1962).

Age Constraints

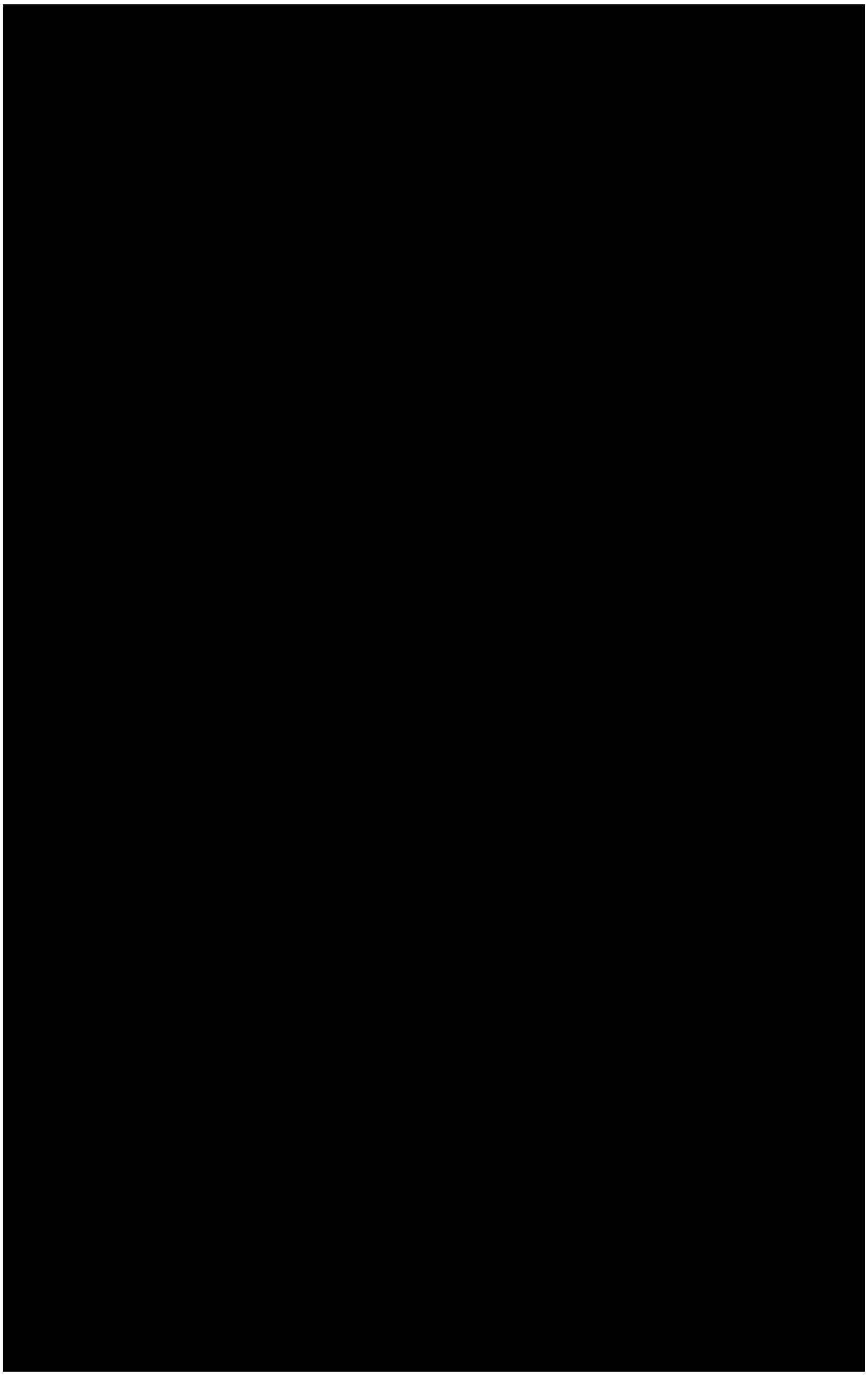
In the presented outcrop two different faunae could be sampled, brachiopods and graptolites (26°03'36,8''S, 67°36'37,8''W). Brachiopods are rare in the Ordovician of the Puna and occur more abundant in the Cordillera Oriental and in the Sierra Famatina or Precordillera (Benedetto and Sanchez, 1996). The brachiopods occur in coarse-grained volcaniclastic conglomeratic greywackes and can be classified as orthides (pers. com. B. Pratt). However, the poor material does not allow a detailed determination (Fig. 5a-b).

The graptolite fauna is represented by several finds of Phyllograptidae, which belongs to the family DICHOGRAPTIDAE Lapworth 1873. *Phyllograptus* sp. (Hall, 1858) occurs from the Arenig up to the Lower Llanvirnian (Fig. 5c). A determination on the basis of species is not possible. *Phyllograptus* sp. could be found in fine-grained sandstones and in conglomeratic volcaniclastic greywackes with grain sizes up to 1.5 cm. Similar graptolites could be found in rocks of the Falda Ciénaga Formation in the Quebrada Carro Grande (Fig. 1a) south-east of the Salar Pocitos (Zimmermann et al., 1998). It could be shown, based on a provenance analysis that the rocks of the latter formation derived from different sources and was deposited in a different tectonic setting, as no volcanic debris could be found in the latter (Zimmermann et al., 2002). We interpret the rocks from Quebrada Carro Grande slightly younger (Llanvirnian), marking the extinction of the synsedimentary volcanic activity in the region (Zimmermann et al., 1998).

Sedimentology

The sedimentary rocks are mainly coarse-grained to silty greywackes and deposited as turbidity currents. Several layers show textures typical for mass-flow or mud-flow deposits comprising shaley rip-up clasts. The rocks show common colors for Ordovician deposits in the Puna like brown-green to yellow-brown. Partly light brown to reddish conglomeratic greywackes occur and white as well as black shale layers. The latter are mostly laminated or structureless. The contacts to the basal part of the lava flows are chilled and thin layers (1-2 mm) of peperites could be observed.

Sedimentary structures are abundant. Normal grading (T_a-T_c and T_c-T_e after Bouma), cross-bedding, lamination as well as slumping are plentiful, the latter especially in the sandy and silty layers. The pelitic units are characterized by a wide heterogeneity of sedimentary structures like



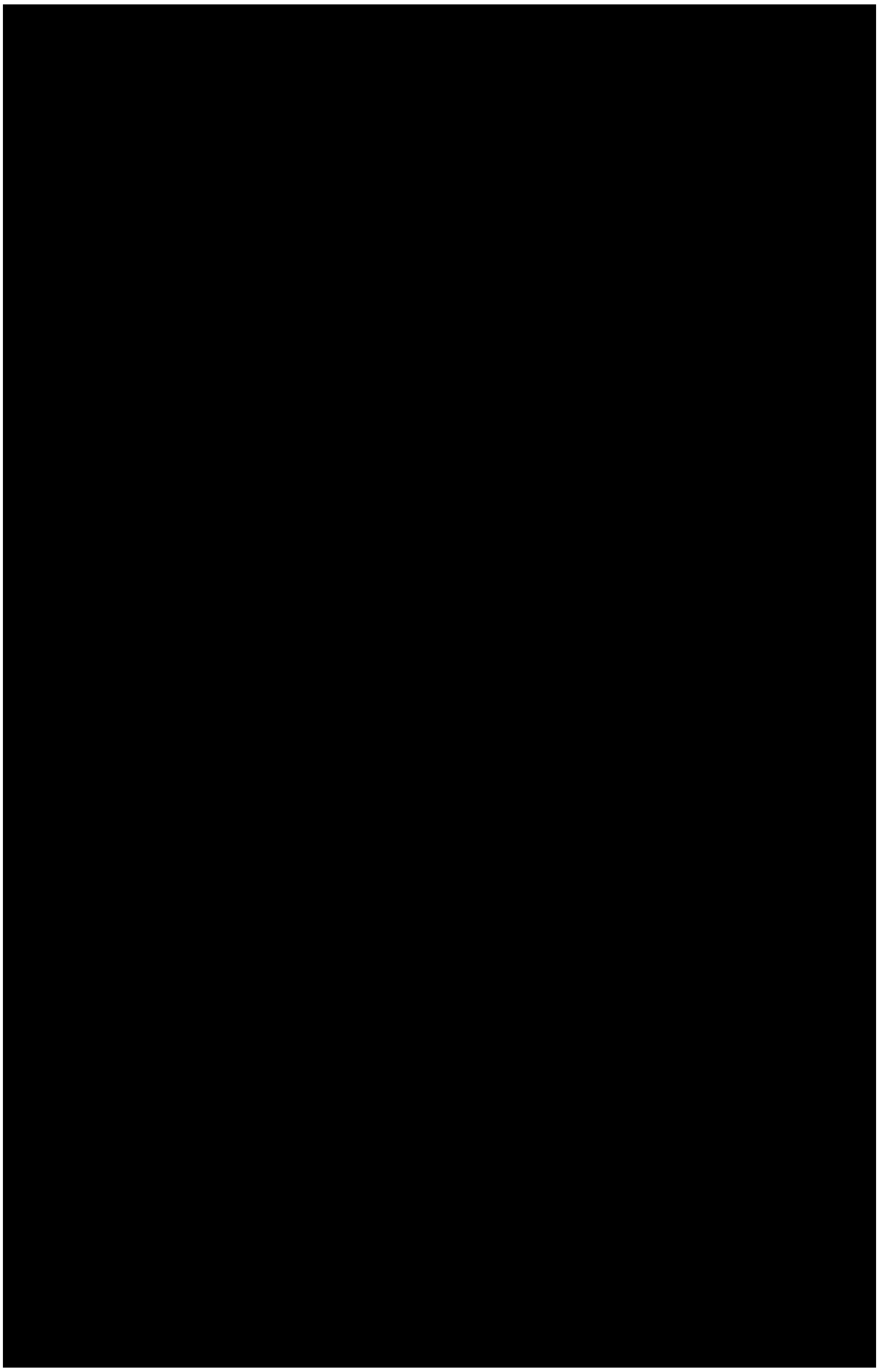


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Table 3: Geochemistry of the sedimentary and volcanic rocks of the Quebrada Diablo (QD) and dacitic rocks of the Sierra de Calalaste (SC) (partly data for the volcanic rocks from Bock et al., 2000). – c= conglomeratic sandstone; m= mudstone; la= litharenite; a= arenite; g= greywacke; r= rhyolite; an= andesite; d= dacite; UCC*= Upper continental crust average after McLennan (2001).

[redacted]

Table 4: Isotope geochemical data for the sedimentary and volcanic rocks in the Quebrada Diablo and interlayered volcanic rocks (data for the volcanites from Bock et al. 2000). Data for the mixing model for the magmatic rocks of the sierras Pampeanas from Rapela et al. (1998), for the Puncoviscana Formation from Bock et al. (2000).

fine-grained turbiditic horizons, cross-beddings and cross-cutting channels. The black shales are only laminated. Flute marks are common and point to a transport axis N to S, orientated to the north. Consequently, the main source area lied to the south of the Sierra Calalaste. However, the relatively immaturity of the rocks points to closely related sources.

Lithotypes

The main characteristic of all lithotypes is a strong volcanogenic component. A significant attribute is the rapid change of lithotypes.

Lithotype 1: volcaniclastic sandstones

Lithotype 1 outcrops sporadically, only at the base of the section, and is strongly weathered to red brown and dark-brown colors. The thickness of the layers ranges between 20 and 80 cm. The rocks are dominated by quartz and alkali feldspar, both rounded to subangular, and mostly intermediate volcanic lithoclasts. Some feldspar grains are strongly altered to sericite and partly to calcite, and could have been plagioclase. The dark-brown matrix (< 10 %) is dominated by clay minerals and quartz. Secondary mica (< 15 µm) shows a preferred orientation related to the cleavage of the rocks. Accessory minerals are chlorite, biotite, muscovite, zircon and hematite. XRD analyses could detect illite as the dominant phyllosilicate in the matrix. Sedimentary structures in this lithotype are rare, only normal grading and laminations could be found. The rocks could have been transported as turbidity currents. However, volcanogenic components are mainly fresh and not broken, derived from close source areas or were transported in high suspension, where quartz occurs as large angular grain or small well-rounded component.

Lithotype 2: volcaniclastic siltstones

This lithotype weathers with blue-green and red-green colors. It occurs dominantly at the base, but is abundant in the whole section, with individual layers between 0,5 and 2m thick. The rocks are composed nearly similar to lithotype 1 but are finer grained. However, feldspars and lithoclasts are more abundant than quartz in these rocks. They comprise sedimentary, quartz-feldspar agglomeratic and intermediate volcanic lithoclasts. The lithotype contains reworked pelitic lenses (0,5cm – 2cm) mostly orientated and elongated in a one direction. This lithotype is affected by three generations of fractures and shows a pronounced cleavage. Sedimentary structures are rare and mainly laminations and wavy bed surfaces occur. The rocks contain impressions of brachiopods and graptolites (*Phyllograptus* sp.).

Lithotype 3: volcaniclastic mudstones

These brown to ochre colored rocks are very hard and break shell-like. Often they are structureless, but partly their sedimentary structures are manifold. They comprise laminations, small channels, cross-bedding, traction carpets, and convolute bedding. The minerals are mainly cryptocrystalline or very fine grained. The determinable grains are mainly angular to subrounded. The thicknesses of the beds vary from 0,5cm to 35cm. Fossils, including microfossils like conodonts or acritarchs could not be detected. In a dark, cryptocrystalline nearly black matrix, small subrounded quartz, feldspar and sedimentary lithoclast grains „swim“ isolated. Muscovite flakes occur as well. The feldspar is mainly plagioclase and always angular but often broken. The feldspar grains are partly sericitised or altered to calcite. Rarely occurs alkali feldspar (sanidine). Lithoclasts are mainly of sedimentary origin, others are strongly weathered and nearly dissolved to „pseudo“matrix and show fine feldspar needles. Furthermore, characteristic for this lithotype are dark, nearly black, cuspate sherds, partly bubble-rich filled with calcite or sericite, mainly fragmented, and a matrix recrystallised to chlorite, a clay mineral or quartz. Secondary occur hematite.

We interpret these layers as reworked and recrystallised ash deposits, which were mixed during the sedimentation with non-volcanic material. However, it is not possible to quantify the amount of volcanic material. Several sedimentary structures point to a reworking as fine-grained turbidites (Lowe, 1982). The fine layering with their partly heterogeneous sedimentary structures point to an depositional area distal to a sub-aqueous fan, in contrast to the higher energetic deposits of lithotype 1 and 4. Especially lithotype 4 (see below) contains several reworked clasts of this lithotype 3, which could point to a progradation into the basin.

Lithotype 4: volcaniclastic greywackes

Lithotype 4 is exposed in the whole section and the most abundant. The rocks are partly light red, but mainly bluish to green-brown. The grainsize varies from silt to very coarse, and can partly be classified as conglomeratic layers. The thicknesses of the beds range from 0,1m to 1,8m, whereas the coarse beds are the thicker ones. In some layers shaley and cherty elongated black lenses (1-30cm) are reworked. The reworked clay lenses show often fine laminations and traction carpets. Silicified clasts are structureless, but elongated. The matrix content varies between 15 and 60%. The rocks are mainly composed of lithoclasts and secondly of feldspar and quartz. Numerous lithoclasts were altered to “pseudomatrix” (Dickinson, 1970) during alteration. This lithotype contains the highest amount of volcanic lithoclasts of all rocks. Most of the clasts show a trachytic texture with strongly altered amphiboles and feldspars, mainly albite and plagioclase. Sedimentary lithoclasts are mainly composed of alkali feldspar and quartz, in some cases up to 3 m large. The feldspars are dominantly sanidine - microcline does not occur - and up to 2 cm large. Feldspars are often sericitised and broken. Some show pertitic segregation textures, what would point to a plutonic origin. Only rarely calcite substitutes feldspar. The few quartz grains show nearly always relicts of a volcanic origin in the form of resorption embayments, which was approved by SEM and BSE (back-scattered electron microscope) analyses. Few quartz grains are undulose or polycrystalline. Accessory mineral are zircon, partly elongated (see below), hornblende and muscovite. Hematite and certain clay-mineral phases are secondary, like small albite needles in the matrix.

The brown-grey to brown-red matrix is partly cryptocrystalline and sericitised. Besides quartz, albite and chlorite as well as small muscovite crystals are abundant. Small feldspar needles and the overall „dirty“ aspect of the matrix could be result of the alteration of volcanic lithoclasts. In some cases such grains are visible as ghoststructures.

Sedimentary structure are very abundant in contrary to the mentioned lithotypes: waveripples, bioturbation, slumping, amalgamation of turbidites, channels, normal gradation, lamination, cross-bedding and convolute bedding and current indicators. Flute marks are NNEW to SSW orientated and direct to the NNE.

In the eastern part of the Quebrada Diablo several brachipode impressions mainly in coarse grained to conglomeratic greywackes could be found. Graptolites are as well abundant, mainly in coarse sand beds of this lithotype. It occurs in the section frequently in intercalation with lithotype 3 and 5. The rocks are poorly sorted and reflect a volcanic source close to the depositional area.

Lithotype 5: silicified rocks

In beds of up to 30cm thickness occur silicified rocks (cherts), which show no sedimentary structures. The whole rock is mainly cryptocrystalline with few undulose quartz grains. They are always angular. XRD analyses show that small amounts of alkali feldspar occur as well as illite. Microfossils could not be identified, excluding an organic origin for the chert. We interpret these layers as primary silicified felsic ashes. Zircons and other heavy minerals could not be found.

Lithotype 6: pyroclastic flows

The beds are relatively thin (30 to 80cm) and not further layered. The rocks show inverse grading, and are white to pink colored. The lithotype breaks shell-like and macroscopically fragmented black clasts (up to 5cm) can be observed. The main components of the rocks are volcanic lithoclasts and quartz. Alkali feldspar is much more abundant than plagioclase, but relatively rare. The volcanic lithoclasts are mainly of intermediate origin, showing trachytic flow structures, and felsic silicified clasts occur sporadically. In the cryptocrystalline silicified matrix dominate fragmented cuspate sherds, which comprise a variety of deformed bubbles. Furthermore, fragmented black clay fragments are elongated and show sometimes fine sedimentary structure in the form of traction carpets (one layer of mainly quartz and feldspar crystals; < 1mm) and laminations. The beds show frequently a wavy surface, rarely wave ripples are possible to identify. Fiamme structures do not occur. Based on the high amount of recrystallised glassy fragments, the unwelded nature, the significant input of epiclastic material into these rocks and the inverse gradation, we interpret this lithotype as a lateral facies of an ignimbrite, probably deposited in a subaquaous environment. At the base of the flows, reworked fragments from the underlying lithotype are nearly always observable. The thin layers of this lithotype support the interpretation that the deposits are mainly a lateral facies of thicker ignimbrites or pyroclastic flows, which are not exposed in the Quebrada Diablo itself.

Lithotype 7: peperites

At the contact of the lava flows to the underlying sedimentary rocks peperites developed. This points to a rapid sedimentation and approves the synsedimentary nature of the volcanism. The top of the lava flows are always eroded, no autobreccias or hyaloclastite layers are preserved. The peperites are strongly altered and show large mainly clastic components, ellipsoidal elongated, which point to a plastic nature of the clasts during the emplacement of the lava flows. The clasts are „swimming“ in a fine cryptocrystalline silicic to volcanic, feldspar needle-rich, matrix. The silicified borders (up to 1cm) of the clasts show an irregular, chertified small alteration rim (1–3mm). The fine rims are intruded by small volcanic matter, in other clasts the chert rims enclose volcanic fragments. The matrix of the peperites shows as well fragmented particles of different lithoclasts. This points to hydroclastic fragmentation. The sediments were deposited mainly in a subaqueous environment, regarding the fossil record, towards a sub-marine deposition. However, hydroclastic volcanic rocks or massive hyaloclastites could not be found in the Quebrada Diablo. Most probably because, those volcanic rocks are easy to erode and probably partly preserved in lithotype 3. Rocks like lithotype 6 and 7 are common in sub-marine volcanic terrains as lateral facies, described elsewhere (e.g. White and Busby-Spera, 1987).

Interpretation of the lithofacies

The Diablo Formation comprises mainly volcaniclastic rocks of different grain-sizes, furthermore cherts (silicified ashes?), peperites and pyroclastic flows, alternating with lava flows. Heterogenic lithofacies of volcanic origin comparable to those are described in volcanic aprons in different localities of different ages (e.g. Breitkreuz, 1986; White and Busby-Spera, 1987; Zimmermann, 2000a). In such depositional environments mainly volcaniclastic debris flows of highly immature nature are deposited (White and Busby-Spera, 1987). Sandy turbidite or in general siliciclastic rocks are rare, but fine-grained turbidites of volcaniclastic composition are abundant (as lithotype 3). The input of intermediate volcanic lithoclasts shows that other volcanic rocks were exposed close to the Quebrada Diablo, but so far not found. However, further to the south (Fig. 1) in the Quebrada Trasmontana dacites and trachyte are observed. These rocks are isolated without any clear contact to adjacent sedimentary rocks. Their preliminary geochemistry points to a continental arc (Zimmermann and van Staden, 2002). Equivalent associations to the Diablo Formation are exposed in the northern Puna at Aguada de la Perdíz and Huaytiquina (described in Bahlburg, 1991). Age equivalent rocks in the Famatina range (Suri Formation) are similar rich in volcanic debris and show a comparable petrography and geochemistry (Zimmermann et al. 2003) and sedimentology (Mangano and Buatois, 1996).

Provenance

Framework minerals

The rocks of the Diablo Formation are dominated by lithoclasts and relatively rich in feldspar with plagioclase as the dominant variety. P/F varies between 0.43 – 0.79 (mean: 0,6) (Table 1). Plagioclase occurs as big clasts (> 1 cm) and many grains have a magmatic zonation. Small plagioclase is rare and strongly altered. Alkali feldspar is represented by sanidine, albite is relatively rare. The sanidine is smaller than the plagioclase and often slightly rounded. The quartz abundances vary between 17,6 and 45,9 %. Undulose quartz and polycrystalline grains are rare. Quartz grains often show resorption embayments pointing to derivation from volcanic sources. The grains are subangular and are poorly sorted (20mm to 1.5 cm). CL analysis shows that more than 80 % of the quartz grains derived from volcanic rocks (Q_{meta}= 2%, Q_{plut}= 13%, Q_{volc}= 85%; n= 450). Quartz originated from metamorphic rocks is nearly absent. The lithoclasts (25,6 – 60,2 %, mean= 45,7; Table 1) are characterized by a high amount of volcanic derived grains, including a notable clast population of intermediate composition with a trachytic texture ($L_{vfelsic}$: $L_{vinterm}$ = 2:1). Basaltic lithoclasts are absent. However, a significant input of sedimentary lithoclasts, fine to medium grained sandstones, can be observed (mean= Ls 64 L_{mm} 5 L_v 31; Fig. 4). Only few greywackes could be found in the population of sedimentary clasts. The few metamorphic lithoclasts are represented by phyllites and meta-sandstones and -greywackes. The matrix varies between 10 and 80% for all lithotypes and comprises quartz, mica and albite. The grains mainly derived from the alteration of mainly volcanic lithoclasts, as the matrix shows always the distribution of fine randomly orientated feldspar needles, and can be interpreted as a “pseudomatrix” (after Dickinson, 1970).

Mainly all lithotype, which could be described under the microscope are immature compositionally as well as texturally. Provenance discrimination diagrams classify the rocks as deposited under the influence of a volcanic arc and a dominant sedimentary continental block source (Fig. 6a).

Heavy minerals

The heavy mineral fraction (60-150mm) is dominated by zircon (mean= 57%; note that these values are based on a sum without opaque minerals), needle-like apatite (mean= 12,6 %) and amphiboles (mean= 18%) (Table 2). Amphiboles are mainly brown, 15% are green. All grains are strongly altered, with irregular crystal boundaries and mainly broken, but sub-angular. Opaque grains (20% of the whole counted heavy minerals) are abundant and mainly represented by hematite. Other heavy minerals are sphalerite, arfvedsonite, barite, augite, pyrite, corundum, pumpellyite, anatas, brookite, dumortierite, topas, lawsonite and prehnite. Turmaline is nearly always brown, often broken and does not show any inclusions. Large broken zircon grains are by most the dominant phase (64%), some euhedral elongated crystals (13 %) could be found with an axis ratio > 3:1, and also a significant amount of well rounded grains (23 %) pointing to a reworking of an older source. Nevertheless, the elongated idiomorphic zircons with gas bubble inclusions can be related to a volcanic origin (Kostov, 1973), as they are not altered with a fresh surface. Prismatic grains are rare, more often occur small pyramidal formed crystals, mainly corroded, subrounded, broken and with a dark nucleus. However, the heavy minerals zircon, tourmaline and rutile dominate the population as the ZTR (after Hubert, 1962) is around 63. The amount of amphibole is notably high and could be related to an intermediate source of a probable volcanic character. The concentration of apatite rises as well regarding the underlying formation, as does the amount of fresh elongated volcanic zircon. The shift in provenance from underlying to the Diablo Formation is obvious, towards a stronger magmatic (volcanic) influence (see Zimmermann and Bahlburg, 2003). Neither metamorphic minerals nor heavy minerals indicating a basic source (e.g. Nechaev and Isphording, 1993; Morton et al., 1992; Schäfer and Dörr, 1997) could be found.

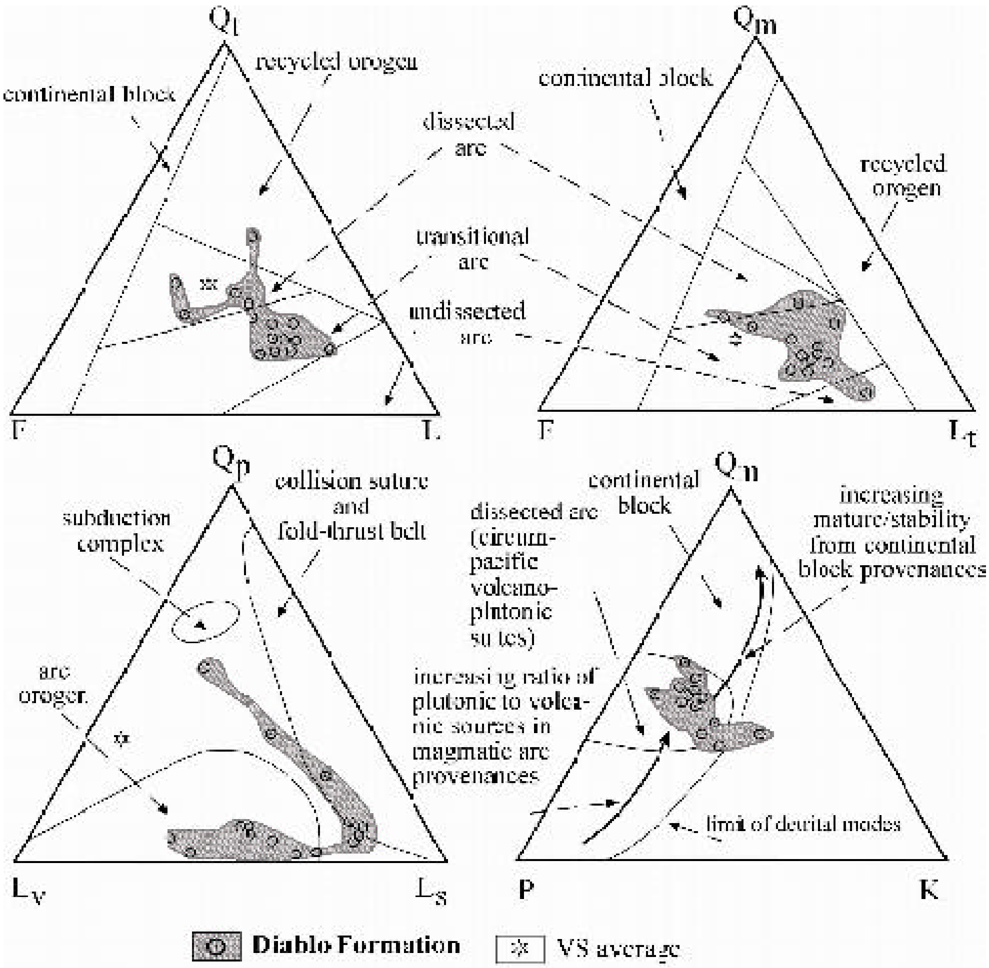

Fig. 6: a) Framework mineral composition of Lower Ordovician sedimentary rocks in the southern Puna. Framework mode diagrams according to Dickinson and Suczek (1979) and Dickinson et al. (1983): Q = quartz, F = feldspar, L = lithoclasts, Q_m = monocrystalline quartz, Q_p = polycrystalline quartz, Q_t = total quartz = Q_m + Q_p, P = plagioclase, K = potassium feldspar, L_t = total lithoclasts incl. Q_p,L_v = volcanic lithoclasts, L_s = sedimentary lithoclasts. For comparisons the average value of the voclanosedimentary successions of the northern Puna are plotted (from Bahlburg, 1990).

Major element geochemistry

The rocks contain a relatively high silica concentration (mean= 72,9; SD= 5,5) related to the high felsic to intermediate volcanogenic component, pointing to a dominance of felsic source composition. The three main alkali elements (Ca, K, Na) vary strongly, probable as a result of their mobility caused by diagenetic processes and fluid activity. Most of the rocks, especially the fine sand to pelitic lithotypes are characterized by lower TiO_2 concentrations (< 0.5 %).

A good measure of the degree of chemical weathering can be obtained by calculating the Chemical Index of Alteration (CIA, Nesbitt and Young, 1982) using the molar proportions of

Al_2O_3, CaO*, Na_2O and K_2O, where CaO* is CaO in silicates only. The resultant value (CIA) is a measure of the proportion of Al_2O_3 versus the mobile oxides in the analyzed samples typically representing the alteration of feldspars and volcanic glass to clay minerals. The rocks of the Diablo Formation comprise a CIA between 50 and 68 with a mean of 56 (Table 3). However, this value is influenced by the occurrence of secondary calcite as replacement for feldspar. The ratio Th/U vs. Th (Fig. 6b) can also be applied successfully in the estimation of the weathering of sedimentary rocks. Both Th and U are relatively immobile and during weathering there is a tendency towards an elevation of Th/U above upper crustal igneous values of 3,5 to 4,0. The reason for this elevation is that U can change its redox state during reworking and is then more easily removable from the system (McLennan et al., 1993). Low Th/U ratios are commonly seen in areas where rapid accumulation and burial of sediment can occur, as it is the case in active margin deposits. However, inherited high Th/U can never be excluded. In Fig. 6b it can be seen that the rocks are partly weathered, where other samples are relatively unweathered. As Th/U ratios can also be inherited from the sources, this can reflect a mixing of fresh volcanic material and older weathered detritus. Relatively low Th/U ratios point to a rapid bury, typical for active margin deposits.

Provenance classification diagrams after Bhatia (1983) and Roser and Korsch (1986) using major element chemistry show a wide spread for the formation and prove that such diagrams cannot be used for provenance interpretations (see Armstrong Altrin and Verma, 2005). This is consistent with the results of Bahlburg (1998) and Zimmermann (2005) obtained from Ordovician rocks of the northern Puna and the Puncoviscana Formation.

Trace element geochemistry

Trace elements like the high field strength elements and REE are particularly useful for characterization of clastic sedimentary rocks as they are extremely insoluble, usually immobile under surface conditions and characterized by a typical behavior during fractional crystallisation, weathering and recycling, thus preserving characteristics of the source rocks in the sedimentary record (e.g. Bhatia and Crook, 1986; Taylor and McLennan, 1985; McLennan 1989; McLennan et al., 1993; Roser et al., 1996).

Generally, the rocks of the Diablo Formation comprise in several elements an UCC (upper continental crust composition) signature (Cs, Ba, V, Cr, Zr, Hf) and are slightly enriched in Yb, Sc and Pb and depleted in Sr, P, Ta, Nb, La (Table 3). Ta, Nb and Ti are depleted in subduction zone related settings, where Pb is normally enriched if continental crust is involved (e.g. Hofmann, 1988, 1997). Table 3 shows the depletion and the slight enrichment clearly. However, absolute element concentrations are difficult to interpret, ratios should be preferred for provenance studies.

Some immobile compatible trace elements like Cr, Ni and V can point to an influence of a basic source, which could be expected especially in volcanic arc terranes. The average Cr content of the upper continental crust is 83 ppm (McLennan, 2001). Two samples of the Diablo Formation have Cr concentrations reaching 200 ppm. However, Cr-bearing minerals were not found in the studied heavy mineral concentrates (60-150mm) but may potentially be present as a minor constituent in the fraction < 60mm. Input from basic sources would also result in an enrichment of V and Ni. The respective values are lower than in the UCC (Table 3) leading to relatively high Cr/V and Y/Ni ratios in most of the samples (Tab. 3). This underlines the absence of such an exotic component in the detrital record (McLennan et al., 1993; Floyd and Leveridge, 1987).

REE pattern in general show only small differences in the concentrations between fine- and coarse-grained rocks (Tab. 3; Fig. 6c). However, most samples of the Diablo Formation are depleted in LREE and enriched in HREE. Sample B44, lithotype 3, interpreted as a volcanic ash, is strongly depleted in LREE (Fig. 5), which may have been caused by the loss of LREE during of weathering of volcanic glass (e.g. Wood et al., 1976; Taylor and McLennan, 1985; Utzmann et al., 2002). However, some samples of the Diablo Formation show only slight negative or positive Eu-anomalies (Fig. 6c; Table 3). This reflects the only relative slight dominance of plagioclase over alkalifeldspar, according to the results of the framework petrography.

Positive Ce_N/Ce^* (where the subscript "N" refers to chondrite normalized abundances; calculation of Ce* after McDaniel et al., (1994)) anomalies point to a strong oxic, negative anomalies to an an-oxic environment, during deposition or in the first case during exposure (e.g. Wilde et al., 1996; Kato et al., 2002). One sample shows high Ce* (1,21; Table 3), while other samples have relatively low values (e.g. 0,68; Table 3). Nevertheless, the mean is more or less typical for UCC (± 1,07, S.D.= 0,14; Table 3) and does not point to a strong oxic or an-oxic environment for the Diablo Formation.

The values of Eu_N/Eu^* (calculation of Eu* after Taylor and McLennan (1985)) for the Diablo Formation are between 0.72 and 1.07 (mean=0.79, SD=0.14; Table 3) and reaching continental arc type values (± 1, according McLennan et al., 1990). The average La_N/Yb_N ratios is about 4.6 in the Diablo Formation (SD= 2,03) and clearly lower than the Post-Archean Australian Average Shale (9,1; after Nance and Taylor, 1976) as a measure for an average crustal composition, reflecting patterns with a less steep slope. However, both indicator point to a strong arc component in the detrital material, thus the volcanic debris can be interpreted as derived from continental arc rocks.

Th/Sc vs. Zr/Sc can be used to reveal the provenance of the detrital mix (e.g. McLennan, et al., 1990). The ratios are ranging between 0,56 and 1,4 (mean= 0.85; SD= 0.32) for Th/Sc and support the mentioned tendency strongly. The rocks of the Diablo Formation scatter from the upper continental crust field to an influence of a less evolved source, which can be interpreted as a continental arc source component. The Zr/Sc ratio is commonly used as a measure of the degree of sediment recycling leading to the enrichment of the stable mineral zircon, and thus Zr, in the deposits (McLennan, 1989; McLennan et al., 1993). The values of the Diablo Formation are ranging between 8.44 and 20.43 (mean= 13.10; UCC= 14.5) and could be interpreted as reflecting a rapid bury without pronounced recycling, according to sedimentary processes in arc terranes.

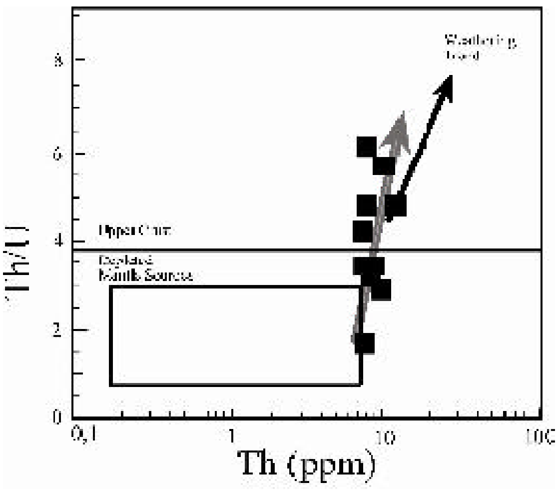

Fig. 6: b) Th/U versus Th to highlight weathering trends (after McLennan et al., 1993). It is notable that some rocks are affected more by alteration than others. The grey arrow emphasizes the weathering trend for the rocks of the Diablo Formation.

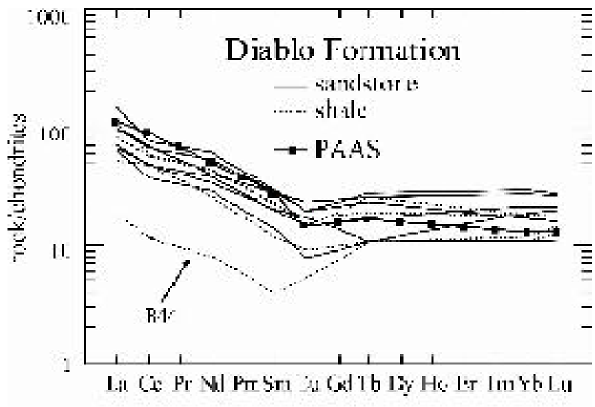

Fig. 6: c) Rare Earth element pattern for the samples of the Diablo Formation (normalized to chondrite after Taylor and McLennan, 1985). Obvious, the loss of light REE in sample B44 interpreted as caused by alteration of glass-rich material.

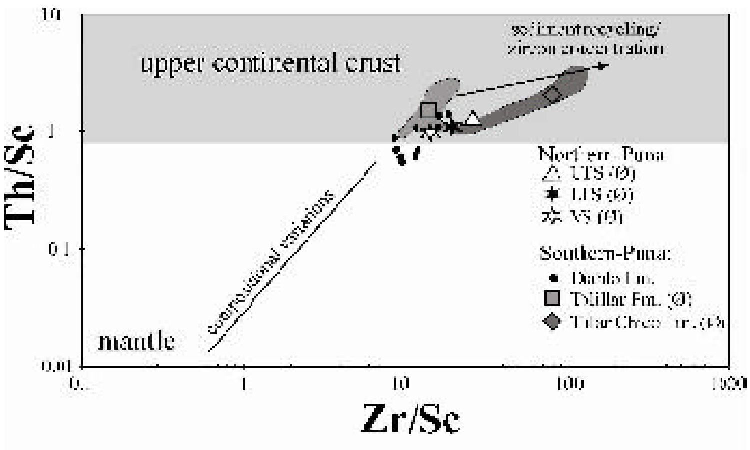

Fig. 6: d) Th/Sc vs. Zr/Sc plot to reveal provenance trends in detrital material (after McLennan et al., 1990). For comparisons average values of Ordovician successions from the northern Puna and southern Puna are shown (see Figure 2 for age constraints). VS= Volcanosedimentary successions; LTS= Lower Turbidite System; UTS= Upper Turbidite System.

Implications of the trace element geochemistry

The volcanogenic Diablo Formation displays a pronounced volcanic arc component using provenance indicating key elements like Ti, Pb, Ta and Nb and ratios as Eu/Eu*, La_N/Yb_N and Th/Sc. Those indicators are typical for an influence of a volcanic arc in the source of the melts for igneous rocks in subduction zones (Hofmann, 1988, 1997; McLennan et al., 1990, 1993), and respectively in sedimentary rocks, where their detrital material is recycled. Variations in the mineralogical record were observed and point to the mixing of different sources, but of continental derivation in a subduction related setting. The REE patterns and the trace element ratios can be best explained by derivation from an evolved volcanic arc of largely UCC composition. This arc influence is most dominant in the Diablo Formation, which is also consistent with the petrographic data. However, the relatively low Eu/Eu* anomaly, coinciding with the petrographic results, points to a relatively shallow melting environment for the magmatic precursors, which were molten in the stability field of plagioclase, as the volcanic rocks are relatively depleted in plagioclase, so are the sedimentary rocks, in an continental arc context. This could support the proposal that the Diablo Formation was deposited in a retro-arc environment.

Isotope geochemistry

Input of detrital material into a basin from different terranes with variable crustal compositions and histories can be distinguished potentially by analyzing the Sr- and Nd-isotope systems of sedimentary rocks (e.g. McCulloch and Wasserburg, 1978; De Paolo et al., 1991; McLennan et al., 1993).

Sm-Nd isotope data are known as less sensitive to low grade metamorphism and their data should give more information about the source rock composition than Sr-isotopes (e.g. DePaolo, 1991). Fig. 7 plots $f_{Sm/Nd}$ (the fractional deviation of the sample $^{147}Sm/^{144}Nd$ from a chondritic reference) of the southern Puna samples versus $e_{Nd(t=470)}$, where $e_{Nd(t=470)}$ is $e_{Nd(t=470)}$ at 470 Ma, the sedimentation age. This allows the simultaneous examination of Sm/Nd and Nd isotope systematics at the time of the sedimentation. The e_{Nd} values (Tab. 4) lie for the rocks of the Diablo Formation on a horizontal to slightly diagonal array framed by $f_{Sm/Nd}$ values between –0.43 and –0.31. The rocks are characterized by an average $e_{Nd(t=sed)}$ value of only -1.95 (Tab. 4) consistent with isotopic data of the synsedimentary lava flows (Table 4) and shows a significant input of less evolved material (also plotted). Such a diagonal array is very typical for arc-related settings as the sedimentary deposits are mostly mixtures of very different sources (e.g. Bock et al., 1994; McDaniel et al., 1994). A diagonal array expresses the different crystallization stages of the Sm/Nd bearing minerals. As one source is the synsedimentary volcanic arc, minerals crystallizing in such an environment would have different e_{Nd} from those derived from an older stable basement, which is incorporated in the detrital record as petrographic studies showed.

The model ages of the Diablo Formation range between 1.2 and 1.4 Ga ($e_{Ndt=sed}$ mean= -1.95; Table 4). They are significantly younger than those of the underlying formations and those of the entire Ordovician stratigraphy of the Puna, as well reflecting the mixture of an older and a younger component, absent in the other Ordovician strata. The interlayered volcanic rocks show nearly similar isotopic characteristics (Fig. 8; Table 4).

A mixing model (after DePaolo et al., 1991) for the Diablo Formation should combine a basement source represented by the Sierras Pampeanas and/or the Puncoviscana Formation with the synsedimentary lava flows of the Diablo Formation itself (data for the mixing model in Table 4). Nd-isotope ratios propose c. 80% felsic to intermediate volcanic material and less than 20% influence of metasedimentary and magmatic basement material. This matches perfectly with the petrographic studies.

Combining the Nd-isotope data with those of the Sr-isotope measurements show a reliable correlation (Fig. 9), even though the Sr-isotope system was slightly disturbed by different deformation phases. Obvious is, that both system do not point to any influence of juvenile material or the mantle. It implies that mainly crustal material was reworked, where a slightly less fractionated component influenced the Nd-isotope system to lower e_{Nd} values represented by the arc magmas.

Finally, we interpret the tectonic setting based on this detailed study for the volcaniclastic succession of the Diablo Formation as being a retro-arc basin, thus on continental crust (Fig. 10a). The synsedimentary volcanic arc lied further to the west.

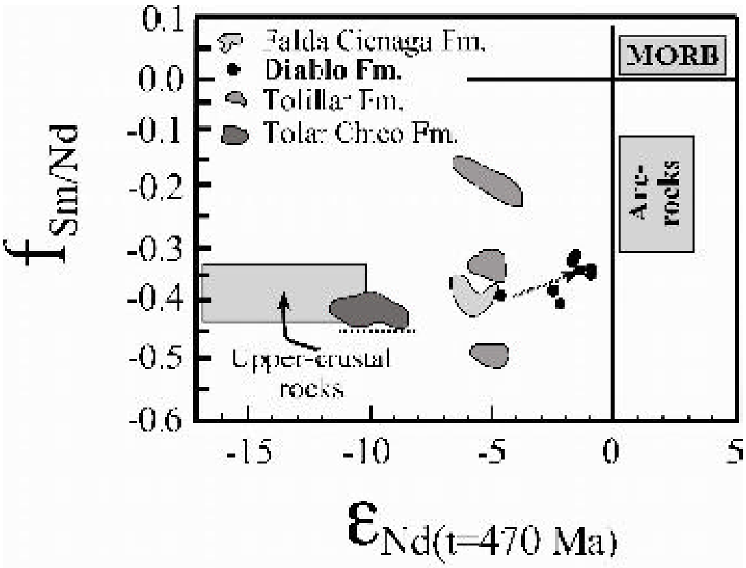

Fig. 7: Plot of $f_{Sm/Nd}$ versus e_{Ndt} for samples from the Ordovician of the southern Puna, where e_{Ndt} is the isotopic composition at the approximate ages of deposition for each formation (see Fig. 2; Table 4). The Diablo Formation shows a typical diagonal array, while samples of the Tolillar Formation are disturbed and show a vertical spread, usually found in magmatic rocks. This points to a redistribution of Nd-isotopes approximately at time of deposition (470 Ma) (Zimmermann and Bahlburg, subm.).

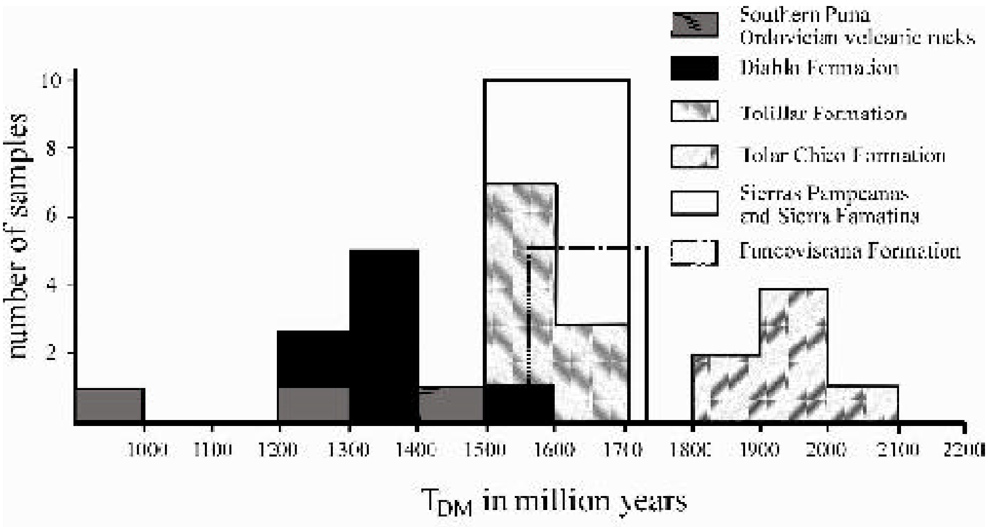

Fig. 8: Histogram of Nd-model ages (T_{DM}) calculated according to the three-stage model of De Paolo et al. (1991) (see Table 4). Included for comparison are data from Late Proterozoic to Cambrian sedimentary and magmatic rocks of Sierras Pampeanas and Sierra Famatina. The samples of the Diablo Formation are characterised by an input of slightly less fractionated, i.e. younger material. The data for the sedimentary coincide with those of the interlayered volcanic beds. Typical model ages of about 1.5 – 1.8 Ga in all formations except the Tolar Chico and Diablo Formations and may indicate a Western Gondwana crustal formation event presented by Sato (1999). Data for the Sierras Pampeanas from Rapela et al. (1998); for the Sierra Famatina from Pankhurst et al. (1998); for the volcanic rocks of the Diablo Formation Bock et al. (2000).

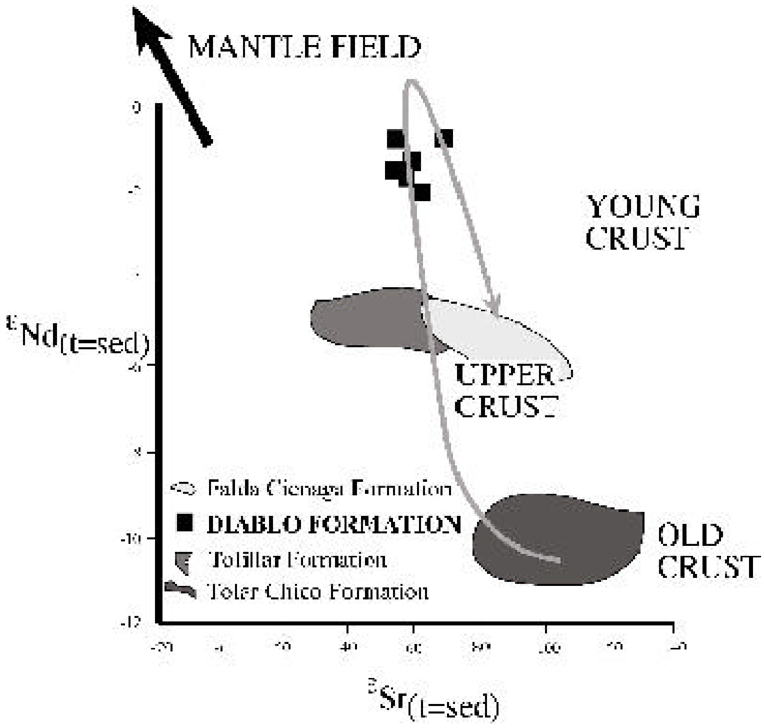

Fig. 9: Epsilon Nd versus Epsilon Sr values for the Ordovician rocks of the southern Puna show a clear trend from older crustal material to the input of younger debris (arc related) and towards the final stage of the basin evolution again the influence of stronger fractionated material. This trend is marked by the thin grey arrow. (after DePaolo and Wasserburg, 1979)

Paleogeographic Implications

As proposed by some authors (e.g. Allmendinger et al., 1983; Ramos et al., 1986; Palma et al., 1990; Conti et al., 1996), the Puna region marks a suture zone between a proposed Antofaal Terrane and the Puna Terrnae or Gondwana. The basin evolution during the Ordovician should reflect such a collisional process combined with the probable obduction of oceanic crust, interpreted as the basic magmatic rocks dispersed in the southern Puna (Fig. 1). Comprehensive provenance studies on supracrustal rocks could not develop arguments in support of this hypothesis (e.g. Bahlburg, 1998; Bock et al., 2000; Zimmermann and Bahlburg, 2003). The existence of a continental volcanic arc during the sedimentation of the Diablo Formation and the absence of volcanic or any basic components in the overlying Falda Ciénaga Formation (Zimmermann et al., 2002) favors a paleotectonic scenario without the addition of exotic material for the Ordovician.

The Diablo Formation, like the Volcanosedimentary Successions in the northern Puna (Huaytiquina and Aguada de la Perdíz, Jama and Sierra de Lina; Fig. 1a) and the Suri Formation in the Sierra Famatina (Fig. 1a) is dominated by volcaniclastic input and the deposition of primary volcanic material with a volcanic arc signature (e.g. Hanning 1986; Breitkreuz et al., 1989; Bahlburg, 1990, Bock et al., 2000; Zimmermann et al, 2003; comp. in Miller and Söllner, 2005). In the early Ordovician, the Puna-Famatinian volcanic arc was built on the western border of the Pampeanas Terrane and a retro-arc basin evolved to the east and northeast of this arc (Bahlburg, 1991; Zimmermann, 2000; Zimmermann and Bahlburg, 2003). In the southern Puna the Diablo Formation represents the climax of volcanic activity during Arenig time. At the Arenig-Lower

Llanvirn transition the volcanic activity ended in the northern and southern Puna (Bahlburg 1990, Bahlburg and Furlong 1996; Moya 1997; Zimmermann et al., 2002). However, the volcanic activity further to the south was more intensive and lasted longer, probably throughout the Llanvirnian. We propose a continuous NW-SE trending volcanic Puna-Famatinian arc, where the Diablo Formation was deposited in the retro-arc basin, probably close to a volcanic centre producing continental arc-related volcanic material (Fig. 10a). Stronger arc related deposits are recognized in the Sierra Famatina (e.g. Clemens and Miller, 1996; Zimmermann et al., 2003) and, if part of Gondwana at this time, in the Cordon de Lila (Fig. 1) in Chile, represented by the Complejo Igneo-Sedimentario de Lila (CISL; Niemeyer, 1989).

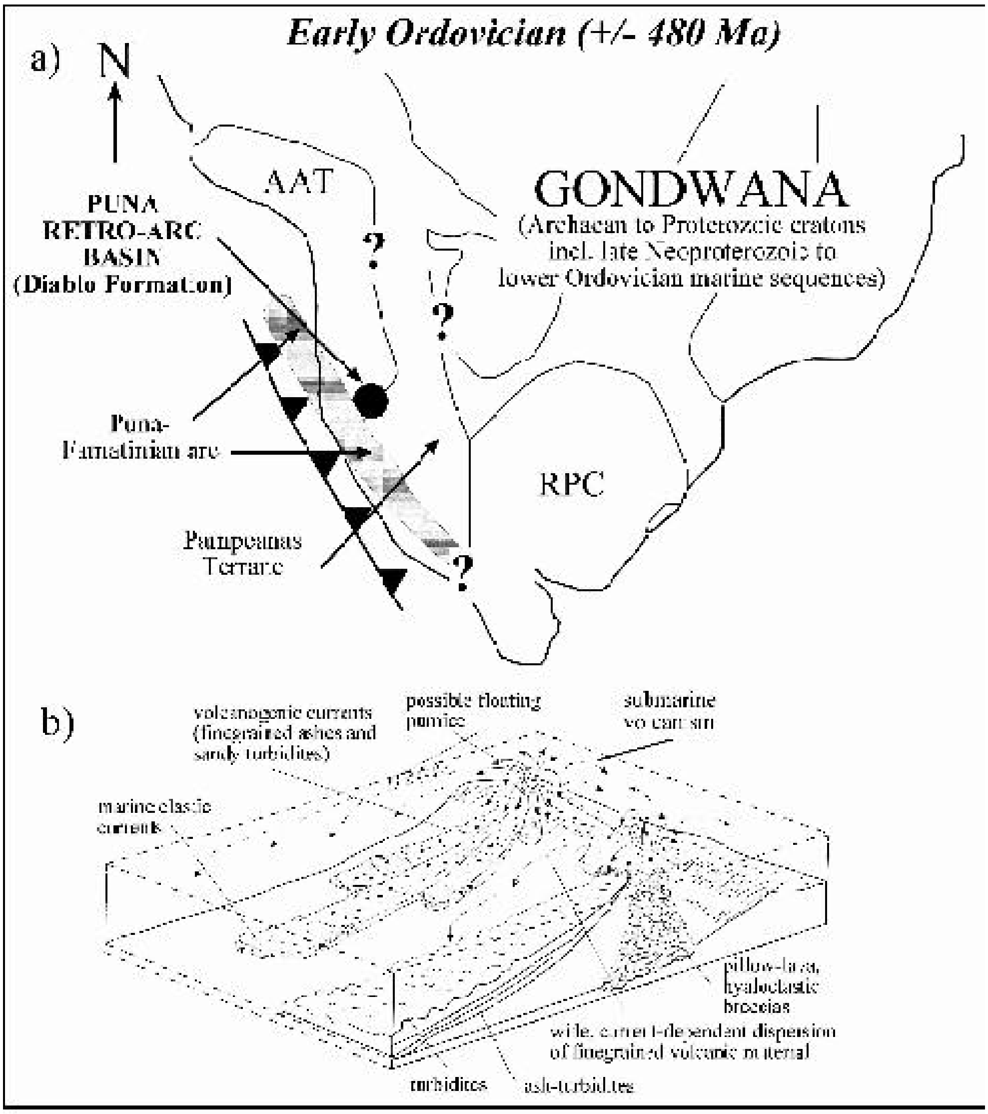

Fig. 10: a) Paleotectonic setting of the Diablo Formation in a retro-arc position to the NW-SE striking Puna-Famatinian arc. (AAT= Arequipa Antofalla Terrane; RPC= Rio de la Plata Craton)– b) Facies model of the Diablo Formation dominated by volcanic material and deposited close to an eruption centre (sketch modified after Einsele, 1992).

Conclusión

The Diablo Formation (*nom. nov.*) is a newly defined volcaniclastic formation, unique in the southern Puna, which was deposited during the Arenig, and can be correlated with the Volcanosedimentary Successions in the northern Puna and with the Suri Formation in the Sierra Famatina to the south.

The compositionally immature detritus of the Diablo Formation contains a high amount of detrital volcanic material. The preservation of mainly fragile volcanic components, subordinated sedimentary and plutonic rock fragments, but to a lesser extent, metamorphic clasts, is indicative for minor weathering, relatively good mixing, and only subsidiary reworking. Such a mixing record cannot be explained in young arc terrains, but easily in retro-arc basins, where different source rocks can be exposed,.

The geochemical composition of the sedimentary rocks is felsic to andesitic and similar to the synsedimentary volcanic rocks. Nd isotope mixing models suggest that detrital material of the synsedimentary lava flows accounts for 80-85 % of volcanic input into the Diablo Formation, assuming that the other mixing end member is represented by the basement of the Pampeanas Terrane and/or the Puncoviscana Formation. This coincides with the petrographical results. The geochemical signature of the sedimentary rocks comprises a "classic" continental arc signature with depletions in Nb-Ta-Ti concentrations, slight enrichment in Pb, high Eu/Eu* values, low La_N/Yb_N and Th/Sc ratios.

The occurrence of graptolites and brachiopods together with sedimentological features, the petrological, geochemical and isotope geochemical similarities of coeval sedimentary and volcanic rocks in this formation indicates that the Diablo Formation formed as a marine volcanic apron close to an eruption center in relatively shallow water below tidal influence. The relatively paucity of plagioclase in an active volcanic arc setting, leads to the assumption that the Diablo Formation was deposited in the retro-arc basin, away from the actual volcanic arc chain, which was most probably NW-SE orientated.

Acknowledgements. This study was funded by the Deutsche Forschungsgemeinschaft grant Ba 1011/11-1, Deutscher Akademischer Austauschdienst grant D/98/04324 as well by the SASOL fund of the Faculty of Science of the University of Johannesburg. We thank R.J. Pankhurst for his constructive comments on the isotopic data, as well as organizing perfect working condition at the NIGL (Keyworth). Fernando Hongn and Cristina Moya were excellent guides during fieldwork. Cristina Moya and Jörg Maletz determined the fossils. The fossils are stored in the fossil collection of the "Universidad Nacional de Salta" in Argentina.

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Appendix:
Analytical Methods

XRD (X-ray diffraction)

15 samples (<2mm) were dried on sample holder (2x2 cm) and measured in 4 directions glycolized and not-glycolized. The source of the Philips X-ray diffractometer was activated with 30 mA and 40kV and the sample were measured from 2 to 45 q in steps of 0.02° per 2 s. The measurements of the illite crystallinity were analyzed using DIFFRAK (Siemens, Version 3.0). The analytical process is described in Warr and Rice (1994). The measurements were carried through at the Department of Geology (Heidelberg, Germany).

SEM (Scanning electron microscope)

Light and heavy minerals were mounted with a special glue on sample holders (diameter 1,2 cm) and coated with gold. The samples were analyzed by a SEM 505 (Philips) with a resolution of 4nm and an activation beam (using a Wolfram kathode) of 15keV at the German Cancer Research Centre in Heidelberg (Germany). Fotos were taken with a Supraflex 56x72 mm (Lindhoff).

CL (cathosoluminescence)

The cathodoluminescence analyses were carried through using ASK-SEM-CL (Firma ASK-Wesel) at the Department of Mineralogy at the University of Heidelberg (Germany). The CL is combined with an EDS-Oxford-Röntgenspektrometer Link Pentafet 7060 with a resolution of 153 eV at 5.9 keV analyzing on a surface of 10 mm^2. The CL analyses were controlled using a BSE-microscope LEO 440 (Firma LEO-Zeiss/Leica-Oberkochem-Cambridge). Polished thin sections were coated in a BALTEC MCS 010 with coal dust in a vacuum of 5,0^{-5} Torr and spreaded with silver.

XRF (X-ray fluorescence)

Analyses for major and trace elements were carried through at the Department of Mineralogy at the University of Heidelberg (Germany) using a SRS 303 (Siemens) wavelength dispersive XRF spectrometer. All measurements are carried out with tube specifications of 50kV and 50 mA. Only fresh and homogeneous samples were selected, crushed to a nominal minus 10 mesh and pulverized in an agate mill to at least minus 150 mesh. Major elements (Fe, Mn, Ti, Ca, K, P, Si, Al, Mg and Na) are determined using fusion disks prepared with 3600 mg Spektroflux 100 (Lithiumborat, $Li_2B_4O_7$) as flux. Spectral overlap corrections are made for Br on Al, Cr on Mn, Al and Ca on Mg, and Mg and Ca on Na. Trace elements are determined on powder briquettes, using Mowiol 2,5% as binding agent in a series of analytical runs using a number of different x-ray tubes. Detection limits for major elements are related to the atomic number between 1 and 10mg for medium heavy elements. Precision is +/- 0,5 (1s), accuracy was controlled by repetitive measurements of standards and each sample was measured two times. The errors of major elements vary between 0,5 – 2 %. First order calibration lines with zero intercept are calculated using six or more international rock standard reference material (SRMs). The data were analyzed using the program grani.quan from Bruker-AXS.

INAA (Neutron activation)

INAA analyzes were made at ACTLABS in Ontario (Canada) via ACME (Vancouver, Canada). Samples were crushed and milled in an agate mill to a fine mesh. The powder was dissolved in lithium metaborate flux fusion and the resulting molten bead is rapidly digested in a weak nitric acid solution. The samples were radiated in a reactor by 7x10^{11} n/cm^{-2}s^{-1}. The emitted g-rays were measured by a highly pure Ge-detector (1,7 keV, 1332 keV ^{60}Co). Detection limits are between 0,5 ppm and 5 ppm for elements like Ag, Cr. INAA precision and accuracy based on replicate analysis of international rock standards are 2-5% (2s) for most elements and +/- 10% for U, Sr, Nd, and Ni.

TIMS (thermal ionisation mass spectrometry)

Sm-Nd analyses were performed at the NIGL (BGS, Keyworth, United Kingdom) by isotope dilution with a mixed ^{149}Sm-^{150}Nd spike, using HDEHP-coated polystyrene columns for the REE separation. Measurements were carried out on a fully automated VG 354 mass-spectrometer, using static collection to determine the Sm and Nd concentrations, and mixed static/peak-jumping to determine the ^{143}Nd/^{144}Nd ratios with an internal precision of +/-10 ppm (1 s.e.m). Long term reproducibility of ^{143}Nd/^{144}Nd ratios both on the La Jolla and in-house standards is better than 15 ppm (1s). Sm/Nd ratios on rock standards are reproducible to 0.1-0.2% (1s). La Jolla standard measured 0.511900 =/-0.000008 of 7 analyses, Nd/NdCHUR=0.512638, Nd/Nd DM=

0.512638, Sm/NdCHUR= 0.1966, $^{147}Sm/^{144}Nd_{crust}$= 0.115, $^{147}Sm/^{144}Nd_{mantle}$= 0.222, $e_{DMt=0}$= 8.6, Q=25.13, f= 0.415, Three stage model Sm/Nd_{limit}= 0.300, equiv. T_{DM}= 2063,1993896236. Nd model ages calculated after DePaolo (1981) and DePaolo et al. (1991).

Recibido: 25 de abril de 2006
Aceptado: 30 de julio de 2006