

Cr-bearing chlorites in low-grade metapelites of the Puncoviscana Formation (Neoproterozoic), Northwestern Argentina

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Chlorites containing appreciable amounts of Cr were recognized by AEM in an anchizonal metapelite of the Puncoviscana Formation during a TEM study. Cr-bearing chlorites are restricted inside a rounded crystal of quartz several microns diameter, they form a group of tabular crystals all with the same crystallographic orientation. AEM analysis reveals Cr contents from 0.07 to 0.25 a.f.u., and a low sum of octahedral cations. Average analysis is $\text{Si}_{3.07}\text{Al}_{1.92}\text{Mg}_{2.62}\text{Fe}_{2.07}\text{Cr}_{0.19}\text{O}_{10}(\text{OH})_8$. Rock-forming chlorites do not contain Cr, a mean formulae based on AEM analyses is $\text{Si}_{2.76}\text{Al}_{2.46}\text{Mg}_{2.43}\text{Fe}_{2.29}\text{Mn}_{0.03}\text{O}_{10}(\text{OH})_8$. This Cr-bearing chlorites are unusual in sediments; their presence in the rock together with chlorites having the usual composition in metapelites is significant regarding the absence of chemical equilibrium in low-grade metamorphic systems.

1. INTRODUCTION

Chlorites containing significant amounts of Cr were identified by AEM in a representative metapelite of the Puncoviscana Formation (1) during a TEM study; sample location is shown in Figure 1. Lattice-fringe images, selected area electron diffraction, and AEM analyses coupled with previous data of white mica crystallinity index (IC), indicate a *state of reaction progress* (2) for Puncoviscana slates consistent with medium anchizonal to epizonal grade metamorphism (3-6). The mineral assemblage of these rocks is mainly quartz, albite, phengite and chlorite.

2. RESULTS

Cr-bearing chlorites are restricted inside a rounded crystal of quartz three microns diameter; they form a group of tabular crystals 260 to 1300 Å thick and 500 to 4200 Å long (Fig. 2), all with the same crystallographic orientation. Micro-diffraction indicates semi-random or random stacking, while lattice-fringe images display scarce interleaved layers at 24 Å and 20 Å in several crystals (Fig. 3). AEM analysis (Table 1) reveals Cr contents from 0.07 to 0.25 a.f.u., and a low sum of octahedral cations. The mean formulae, based on AEM analysis, is $\text{Si}_{3.07}\text{Al}_{1.92}\text{Mg}_{2.62}\text{Fe}_{2.07}\text{Cr}_{0.19}\text{O}_{10}(\text{OH})_8$.

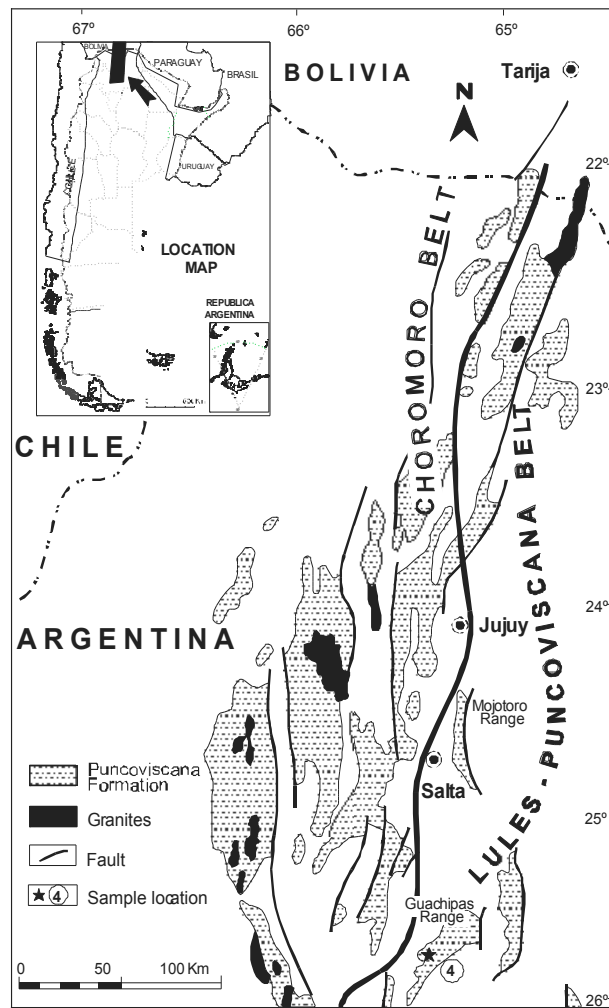


Figure 1. Outcrops of Puncoviscana Formation with sample location (see star).

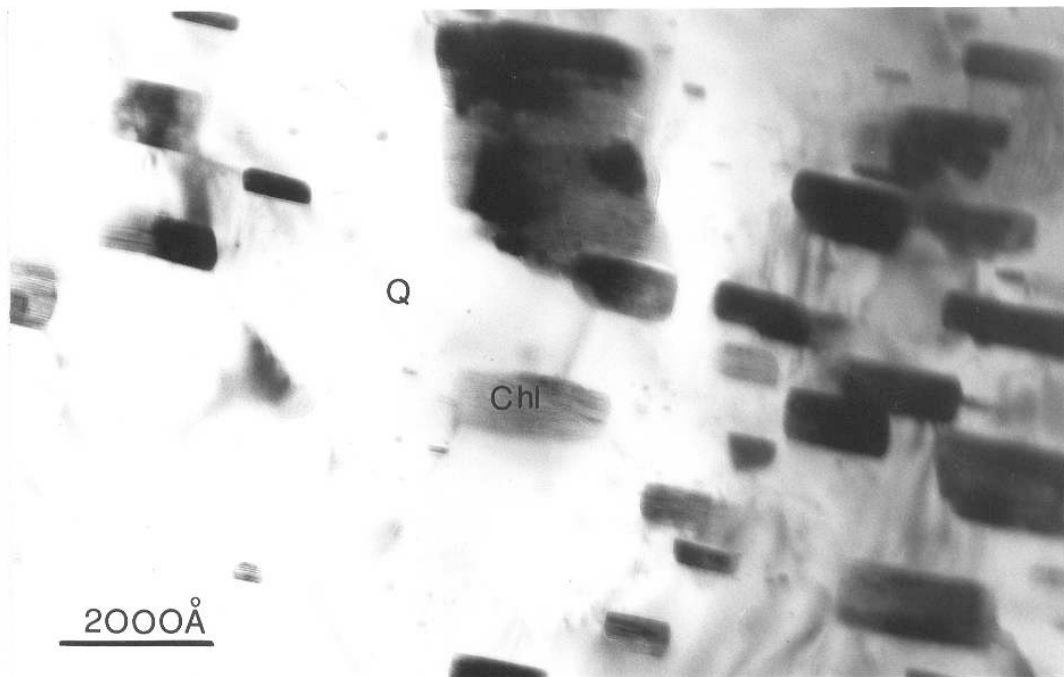


Figure 2. Textural image of Cr-bearing chlorites inside a quartz grain.

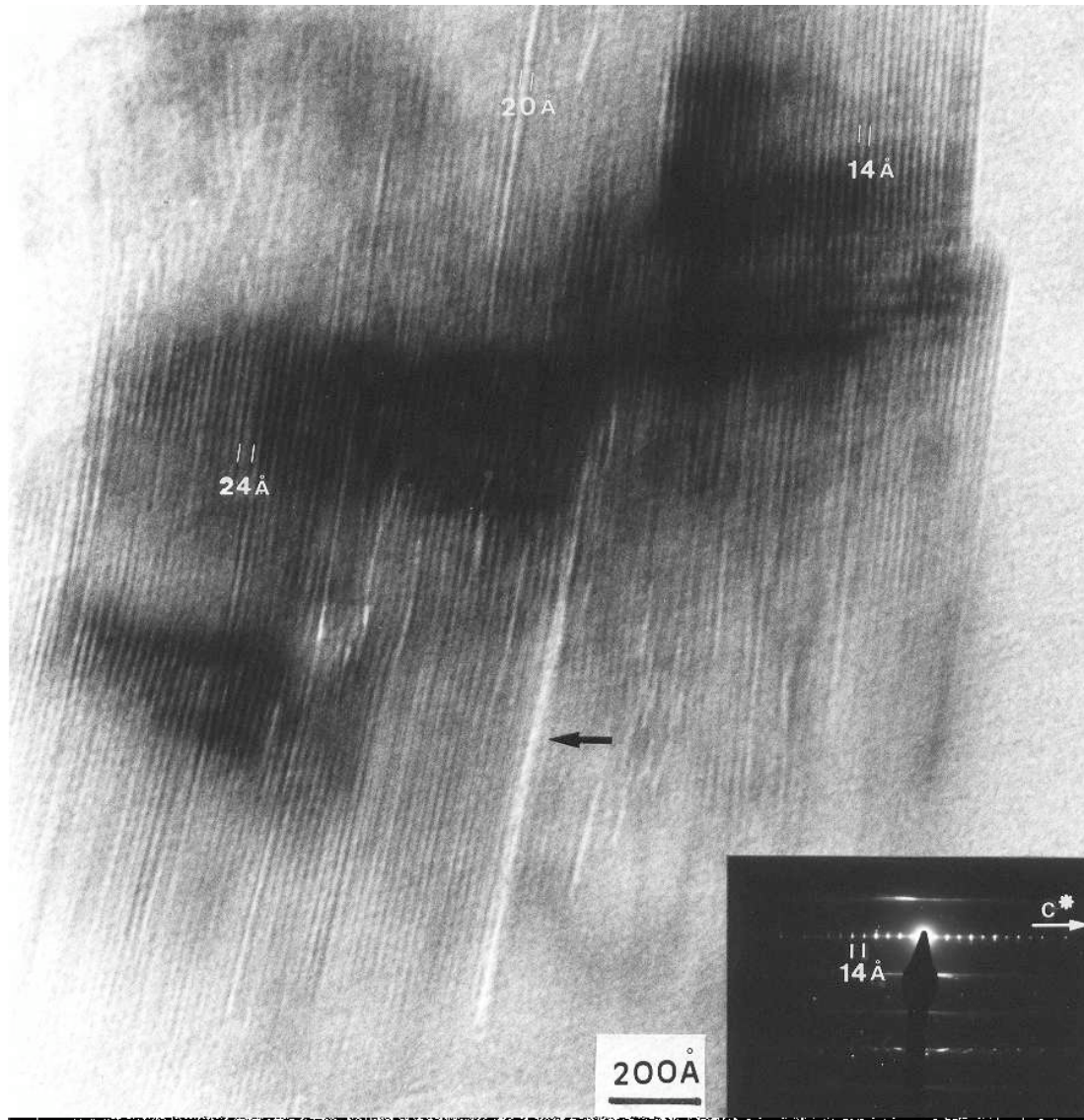


Figure 3. SAED pattern of semi-random Cr-bearing chlorites and corresponding lattice fringe image.

IC of $0.30 \Delta^2\theta$ and a **b** parameter of 9.035 \AA were measured for metapelite PU4. Phyllosilicates of this sample appear in TEM images in packets with straight and continuous lattice fringes. More common crystalline defects are low-angle boundaries between packets of the same mineral (Fig. 4) or between mica and chlorite packets. 2M polytype was identified in all the dioctahedral micas analyzed. Muscovite occurs as defect-free packets some 40-350 layer thick. Bulk sample chlorite exhibit semi-random and ordered stacking in SAED patterns. Among ordered chlorites one (Fig.4, inset) and two layer sequences were recognized. Ordered as well as semi-random chlorite show straight and continuous 14 \AA and occasionally 28 \AA lattice fringes (Fig. 4). Chlorite of the bulk sample do not contain Cr (Table 1) and the mean formulae, based on AEM analyses, is $\text{Si}_{2.76}\text{Al}_{2.46}\text{Mg}_{2.43}\text{Fe}_{2.29}\text{Mn}_{0.03}\text{O}_{10}(\text{OH})_8$. Smectite,

identified at TEM scale, was interpreted as a retrogradation product of previous phyllosilicates (6).

3. DISCUSSION

It is well known that chlorites easily reach chemical equilibrium with the system; furthermore it is frequent that chemically equilibrated chlorites coexist in low-grade metamorphic rocks with metastable micas that are far from equilibrium (e.g. 7). Nevertheless Cr-bearing chlorites in PU4 metapelite are not equilibrated with the rock-forming chlorites. In this case the impossibility that fluids reached these detrital chlorites due to the preservation by the quartz grain has been determinant to allow them to maintain their original composition and texture. The concept of state of reaction progress is now fundamental in the understanding of the diagenetic and low-grade metamorphic processes (2) as it assumes the general lack of equilibrium and the metastable character of most of the mineral phases generated by these geological processes. Therefore the usual grade-indicators reflect more the kinetic than the thermodynamic state of evolution. From this point of view very local factors, as permeability or the existence of physical barriers for fluids, are highly determinant of the mineral chemistry in low-grade rocks.

The first indication of the coordination of Cr^{+3} in chlorites comes from crystal field theory that suggests that this cation has a large preference for octahedral coordination (8). Afterwards structural refinements of Cr-bearing chlorites carried out by Phillips and co-workers (9) determined that Cr^{+3} was concentrated in the interlayer octahedral site M(4). The studied Cr-bearing chlorites present a low sum of octahedral cations that are compatible with Cr^{+3} replacing dioctahedral cations in octahedral sites. This replacement is also compatible with the amount of positive charge required to balance the negative charge due to substitution of $^{\text{IV}}\text{Al}$ for Si in tetrahedral sheets.

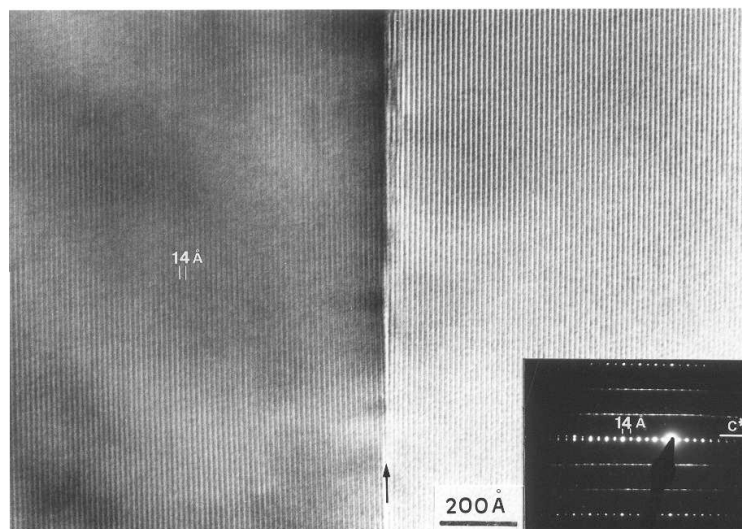


Figure 4. SAED pattern (inset) of 1-layer polytype chlorite and corresponding lattice fringe image showing a thick defect-free packet. Arrow indicates low angle boundaries.

Table 1
AEM analyses of Cr-bearing and bulk sample chlorites

Element	Cr-bearing			Bulk sample		
	PU4-3	PU4-4	PU4-5	PU4-6	PU4-7	PU4-10
Si	2.84	3.17	3.19	2.70	2.57	3.01
^{IV} Al	1.16	0.83	0.81	1.30	1.43	0.99
^{VI} Al	1.15	0.93	0.89	1.19	1.17	1.31
Mg	2.40	2.75	2.72	2.42	2.29	2.57
Fe	2.35	1.89	1.97	2.37	2.53	1.96
Ti	-	-	-	-	-	-
Mn	-	-	-	0.04	0.07	-
Cr	0.07	0.26	0.25	-	-	-
Σ_{oct}	5.97	5.82	5.83	6.02	6.06	5.84
K	-	-	0.01	-	-	-
Ca	-	-	-	-	-	-

REFERENCES

1. J.C.M. Turner, Estratigrafía de la Sierra de Santa Victoria y adyacencias. Boletín Acad. Nac. Ciencias, Córdoba, 41 (1960), 163.
2. R.J. Merriman and D.R. Peacor, Very low-grade metapelites: mineralogy microfabrics and measuring reaction progress. In: Low-grade metamorphism, Frey, M. & Robinson, D. (eds), Blackwell Science, Oxford, 1999.
3. M. Do Campo, F. Nieto and R. Omarini, Mineralogía de arcillas y metamorfismo de la Formación Puncoviscana en localidades de la Cordillera Oriental y Puna, Argentina. *X Congr. Lat. Geología*, Buenos Aires. Actas 2, 217 (1998)..
4. M. Do Campo, Metamorfismo del basamento en la Cordillera Oriental y borde oriental de la Puna. In: Relatorio de la Geología del Noroeste de Argentina, González Bonorino, G., Omarini, R. & Viramonte, J. (eds), Universidad de Salta, Salta, 1999.
5. M. Do Campo, Mineralogía, geoquímica y geocronología de la Formación Puncoviscana (Neoproterozoico) entre los 23°30' y 25°50' de Latitud Sur, Noroeste de Argentina. Ph Thesis (unpublished). Buenos Aires University, 1999.
6. M. Do Campo and F. Nieto, Transmission Electron Microscopy study of very low-grade metamorphic evolution in Neoproterozoic Pelites of the Puncoviscana Formation (Cordillera Oriental, NW Argentina), *Clay Miner.* (in press).
7. G. Giorgetti, I. Memmi, and F. Nieto, Microstructures of intergrown phyllosilicate grains from Verrucano metasediments (northern Apennines, Italy). *Contr. Mineral. Petrol.*, 128 (1997) 127.
8. R. G. Burns, *Mineralogical Applications of Crystal Field theory*. Cambridge University Press, Cambridge, 1970.
9. T.L. Phillips, J.K. Loveless and S.W. Bailey, Cr⁺³ coordination in chlorites: a structural study of ten chromian chlorites. *Am. Miner.*, 65 (1980) 112.