

GEOLOGICAL NOTE

Garnet composition from the Reflejos de Mar LCT-pegmatite, Ancasti district, Argentina and its implication for exploration of primary deposits of lithium

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ABSTRACT. The Reflejos de Mar Li-pegmatite, located in northwestern Argentina, is part of the Villismán pegmatite group, Ancasti District, Pampean Pegmatite Province. Four garnet crystals from the outermost part of the pegmatite were analyzed by major and minor elements (SiO₂, TiO₂, Al₂O₃, Cr₂O₃, MgO, CaO, MnO, FeO) using electron microprobe. The pegmatite belongs to the rare-element class, spodumene type, LCT (Li-Cs-Ta) petrogenetic family. Based on their Mn and Fe contents, the analyzed garnet can be assigned to the spessartine-almandine serie. The cores and rims of the analyzed garnets show significant differences for the divalent components in VIII-coordination, especially, Mn and Fe. The average MnO and FeO contents in the cores of the grains is 34.6 and 8.29 wt%, respectively, while in the rims is 29.31 and 12.95 wt%, respectively. The Fe/Mn ratio at the core of the grains is 0.24 while at the rims it is 0.44. Cr₂O₃ and TiO₂ contents are very low (<0.17 wt%) and the values of SiO₂ and Al₂O₃ are ~36 and ~21 wt%, respectively. The mean chemical and molecular formulas of the core can be expressed: [(Mn_{2.40} Fe_{0.57} Ca_{0.02} Mg_{0.02})_{3.01} (Al_{1.99} Cr_{0.002})_{2.00} (Si_{2.99} Ti_{0.01})_{3.00} O₁₂]; {Sps_{79.8} Alm_{18.9} Grs_{0.7} Prp_{0.5}}; and the rim as: [(Mn_{2.04} Fe_{0.89} Ca_{0.05} Mg_{0.04})_{3.02} (Al_{2.00} Cr_{0.002})_{2.00} (Si_{2.98} Ti_{0.005})_{3.00} O₁₂]; {Sps_{67.6} Alm_{29.5} Grs_{1.6} Prp_{1.3}}. The chemical composition of garnet from the Reflejos de Mar pegmatite is similar to other worldwide examples in similar rocks, especially LCT pegmatites, which are highly evolved and associated with Li mineralization. Therefore, its composition could be used as an additional tool in the exploration of Li-bearing pegmatites in the Pampean Pegmatite Province. The differences in Fe-Mn contents between core and rim of the crystals would be controlled by variations in composition of the pegmatitic melt and, in addition, by the simultaneous precipitation of other mineral phases, for example, schorl and Mn-Fe-bearing phosphates.

Keywords: Spessartine-almandine, LCT-pegmatite, Villismán group, Ancasti district, Sierras Pampeanas

RESUMEN. Composición del granate de la pegmatita LCT Reflejos de Mar, distrito Ancasti, Argentina, y su implicancia en la exploración de depósitos primarios de litio. La pegmatita Reflejos de Mar, ubicada en el distrito Ancasti de la Provincia Pegmatítica Pampeana (PPP), en el noroeste de Argentina, pertenece a la familia LCT (Li-Cs-Ta). Mediante microsonda electrónica, se determinaron los contenidos de elementos mayores y minoritarios (SiO₂, TiO₂, Al₂O₃, Cr₂O₃, MgO, CaO, MnO, FeO) del centro y borde de cuatro cristales de granates provenientes de una muestra extraída de la zona más externa de la pegmatita. De acuerdo con sus contenidos de Mn y Fe, los granates son asignados a la serie espesartina-almandino. Los centros y los bordes de los cristales analizados tienen similares valores de SiO₂ y Al₂O₃, ~36 y ~21%, respectivamente, mientras que los contenidos de Cr₂O₃ y TiO₂ son muy bajos (<0,17%). El mayor contraste

entre el borde y centro de los cristales lo presentan los componentes divalentes en coordinación VIII, especialmente Mn y Fe. Los contenidos promedio de MnO y FeO en los centros de los granos son de 34,6 y 8,29% peso, respectivamente, mientras que en los bordes son 29,31 y 12,95% peso, respectivamente. La relación Fe/Mn en el centro de los granos es 0,24, mientras que en los bordes es de 0,44. La fórmula química del centro de los granos analizados puede ser expresada como $[(Mn_{2,40} Fe_{0,57} Ca_{0,02} Mg_{0,02/3,01} (Al_{1,99} Cr_{0,002/2,00} (Si_{2,99} Ti_{0,01})_{3,00} O_{12})]$ y la fórmula molecular como $\{Sps_{79,8} Alm_{18,9} Grs_{0,7} Prp_{0,5}\}$. A su vez, la fórmula química de los bordes es $[(Mn_{2,04} Fe_{0,89} Ca_{0,05} Mg_{0,04/3,02} (Al_{2,00} Cr_{0,002/2,00} (Si_{2,98} Ti_{0,005})_{3,00} O_{12})]$ y la fórmula molecular es $\{Sps_{67,6} Alm_{29,5} Grs_{1,6} Prp_{1,3}\}$. La composición química obtenida para el granate de la pegmatita Reflejos de Mar es similar a la de otros ejemplos en el mundo en rocas similares, especialmente de pegmatitas LCT altamente evolucionadas asociadas con mineralización de litio. Esto nos permite sugerir que la composición del granate en las pegmatitas puede ser utilizado como una herramienta adicional, en la exploración de pegmatitas mineralizadas con Li en la PPP. Las diferencias composicionales de Mn y Fe entre el centro y el borde de los cristales podrían estar vinculadas a variaciones en la composición del magma pegmatítico y, adicionalmente, por la cristalización simultánea de otras fases minerales, tales como chorlita y fosfatos portadores de Mn y Fe.

Palabras clave: Espesartina-almadino, Pegmatita LCT, Grupo pegmatítico Villismán, Distrito Ancasti, Sierras Pampeanas.

1. Introduction

Garnet forms a very extensive and complex supergroup that includes isostructural minerals, but it is also a group with the same name within this same supergroup (Grew *et al.*, 2013). Following these authors, the garnet group can be represented by the chemical formula: $X_3Y_2Z_3\phi_{12}$, where X and Y are mainly divalent cations in VIII-coordination such as Fe^{+2} , Ca, Mg and Mn, and trivalent cations in VI-coordination such as Al, Fe^{+3} and Cr, respectively, while Z is occupied by tetravalent cations, fundamentally Si, in tetrahedral coordination; ϕ is essentially O, but also, in a few cases, OH and/or F (*e.g.*, Geiger and Rossman, 2020). According to the dominant cation that occupies the position of both X and Y in the isometric structure of the mineral, the group is divided into the following species: pyrope (Prp; Mg^{+2} , Al^{+3}), almandine (Alm; Fe^{+2} , Al^{+3}), spessartine (Sps; Mn^{+2} , Al^{+3}), grossular (Grs; Ca^{+2} , Al^{+3}), andradite (Adr; Ca^{+2} , Fe^{+3}), and uvarovite (Uv; Ca^{+2} , Cr^{+3}) (*e.g.*, Grew *et al.*, 2013).

Concerning its occurrence, garnet is a common accessory mineral in a wide range of crystalline rocks (igneous and metamorphic) and as detritus in sedimentary rocks (Deer *et al.*, 1997; Alderton, 2020). The chemical composition of the mineral is used in the first group of rocks for petrogenetic implications, including thermobarometry (*e.g.*, Deer *et al.*, 1997; Alderton, 2020), while in the second group of rocks, for information on provenance of sediments (*e.g.*, Mange and Morton, 2007).

Garnet is also present extensively in pegmatites and aplites of different classes and degree of magmatic evolution, but especially in those originating from

aluminous sources (LCT family), where it is associated with minerals such as muscovite and tourmaline (London, 2008; Maner *et al.*, 2019). In these pegmatitic systems, the predominant composition of garnet is spessartine and, to a lesser extent, almandine (Černý *et al.*, 1985; Sokolov and Khlestov, 1990; London, 2008; Muller *et al.*, 2009; Hernández-Filiberto *et al.*, 2021; Sousa *et al.*, 2021).

The chemical composition of garnet from granitic pegmatites is useful for various geological applications such as an important tool to elucidate trends in petrogenesis and magmatic evolution (Černý *et al.*, 1985; Nakano and Ishikawa, 1997; London, 2008; Javanmard *et al.*, 2018; Sami *et al.*, 2020; Hernández-Filiberto *et al.*, 2021; Sousa *et al.*, 2021; Yu *et al.*, 2021), identifying geochemical and geological characteristics of processes and reactions in magmatic/hydrothermal/metasomatic environments (London, 2008; Nejbart *et al.*, 2018; Yu *et al.*, 2021), as a tool for mineral exploration in pegmatites (Sokolov and Khlestov, 1990), especially those Li-bearing (Heimann *et al.*, 2012; Moretz *et al.*, 2013; Heimann, 2015) and even applications in gemology (Laurs and Knox, 2001).

The objective of this work is to reveal the chemical composition of the core and the rim of four garnet crystals from the outermost zone of the Reflejos de Mar pegmatite located in the Ancasti District of the Pampean Pegmatite Province (PPP) in northwestern Argentina. From these data, we aim to evaluate the use of garnet composition in the exploration for Li bearing pegmatites in the PPP and, in addition, to obtain information concerning the magma from which these rocks were formed.

2. Regional and local geological setting

The Pampean Pegmatitic Province (PPP) contains several districts of different mineralogical paragenesis, geochemical signature and age (Galliski, 1994, 2009). Pegmatites of the Muscovite and Rare Element classes predominate, including within these, the LCT (Li-Cs-Ta) and NYF (Nb-Y-F) families according to the classification of Černý and Ercit (2005). The pegmatites of the PPP are hosted in crystalline rocks (igneous and metamorphic) mainly of Early and Late Paleozoic age, in the geological province of the Sierras Pampeanas, in the central and northwestern sector of Argentina (e.g., Toselli *et al.*, 1986, 2007; Pankhurst *et al.*, 2000; Rapela *et al.*, 2001; Rossi *et al.*, 2002; Miller and Söllner, 2005; Dahlquist *et al.*, 2006, 2013).

The Ancasti pegmatitic district is part of the PPP located in the homonymous mountain-range (Galliski,

1994). The Sierra de Ancasti has a predominantly N-S orientation and is located in the southeast sector of the Catamarca province, Argentina (Fig. 1A). It is composed of metamorphic rocks of medium and high metamorphic grade, including phenomena of partial melting (anatexis). The protolith was siliciclastic sedimentary rocks and to a lesser extent calcareous, deposited in a marine basin (Miller and Willner, 1981; Aceñolaza *et al.*, 1983; Willner, 1983).

The metamorphic rocks of the Sierra de Ancasti are intruded by small plutons and stocks, mainly of granitic composition and Paleozoic age, although the magmatic peak would have taken place during the Lower and Middle Ordovician (Knüver, 1983; Toselli *et al.*, 1983, 2011; Cisterna, 2003; Dahlquist *et al.*, 2011, 2012; Rzyziuk *et al.*, 2014; Marangone *et al.*, 2020).

The Ancasti pegmatitic district contains pegmatites, generally with zoned internal structure and of

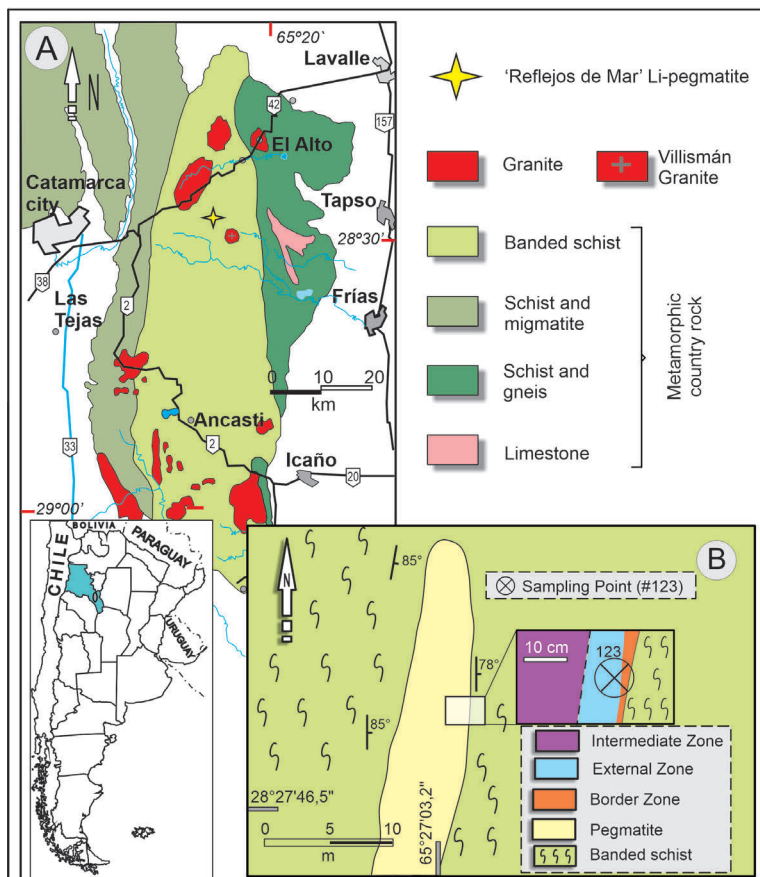


FIG. 1. **A.** Simplified geologic map of the northern part of the Sierra de Ancasti, Argentina showing the location of the Reflejos de Mar Li-pegmatite, modified of Marangone *et al.* (2020). **B.** Detailed map of the northern area of the Reflejos de Mar Li-pegmatite, modified of Sardi *et al.* (2017).

different mineral paragenesis. They mainly intrude metamorphic rocks, and to a lesser extent also granitic rocks (Lottner, 1983). Galliski (1999) recognized pegmatitic groups with main paragenesis of Be- and Li- rich minerals, one of them being the Villismán pegmatitic group in the north-central sector of the mountain-range.

The mineralogy of the pegmatites in this district includes K-feldspar, quartz, and plagioclase as essential minerals and muscovite, biotite, beryl, garnet, spodumene, tourmaline, triplite, triphylite-lithophyllite, amblygonite-montebrazite, apatite, and zircon as accessory minerals (Galliski, 1999). The pegmatites of the Sierra de Ancasti can be classified as belonging to the class of rare elements and to the beryl, spodumene or albite-spodumene types (Galliski, 1994, 1999; Galliski *et al.*, 2022) according to the classification of Černý and Ercit (2005).

3. The Reflejos de Mar Li-pegmatite

It forms part of the Villismán pegmatite group (Fig. 1B) and its coordinates are 28°27'21" S and 65°26'55" W. The pegmatite host rocks are schists and the contacts are sharp and concordant with the regional structure of the metamorphic rocks. In some sectors tourmalinization of the host rock occurs.

The lithology of the host rocks of the Reflejos de Mar pegmatite consists essentially of banded schists and mica-schists with lens-like intercalations of quartz micacites and calc-silicate rocks (Aceñolaza and Toselli, 1977). Banding subparallel to the original stratification in the schists is represented by an intercalation of clear layers rich in quartz and feldspars and very high amount of mica; and dark layers, composed mainly of biotite, in addition to muscovite and accessory minerals.

The pegmatitic body is tabular in shape with an approximate N-S strike and a vertical to subvertical dip. The length of the body can reach about 75 m and the average thickness is about 4 m (Sardi *et al.*, 2017). The internal structure of the pegmatite shows symmetrical zoning (Herrera, 1964; Fernández Lima *et al.*, 1972), with the transitional contacts between the different zones. The grain size increases successively from the border to the core of the body (Sardi *et al.*, 2013).

The outermost zones of the pegmatite are constituted by the border and external zones

defined by Sardi *et al.* (2017). The first is in direct contact with the host rock, with a thickness of a few centimeters, and is sometimes absent. The texture is equigranular, fine- to very fine-grained, composed of quartz, K-feldspar (microcline), plagioclase and muscovite. Fernández Lima *et al.* (1972) described in addition zircon, tourmaline, apatite, and topaz. The external zone has a greater thickness and grain-size. Cleavelandite appears abundantly in this zone with a composition determined by Fernández Lima *et al.* (1972) of $An_{0.5}$. Accessory minerals in this zone are tourmaline, zircon, rutile, spessartine, spodumene and beryl, and scarce sillimanite (Herrera, 1964; Fernández Lima *et al.*, 1972). The intermediate and central zones are considered the innermost zones of the body. The first one is more developed of the body reaching up to 4 m thick and contains abundant accessory minerals, some of which are extraordinarily large, *e.g.*, 1.5 m or more (Sardi *et al.*, 2017). It is composed of quartz and albite (cleavelandite variety) and scarce perthitic microcline; accessory minerals include spodumene, muscovite, apatite, beryl, garnet. Fernández Lima *et al.* (1972) also recognize lithiophilite and sillimanite. The central zone is about 2 m thick and shows the largest granulometry of the body with some crystals with more than 1 m in length (Sardi *et al.*, 2013), composed essentially of quartz, spodumene and albite (cleavelandite). Particularly for the Reflejos de Mar pegmatite, Galliski *et al.* (2022) add as accessory minerals, columbite-tantalite group minerals, triplite, triphylite and amblygonite.

4. Materials and methods

The analyzed garnets are from a single sample from the external zone of the Reflejos de Mar pegmatite of the Villismán Pegmatite Group, very close to the host rock. They appear grouped in very small masses no larger than 2 cm across, associated with quartz and feldspars. The shape of the garnets is idiomorphic and subidiomorphic, somewhat tabular in sectors. They appear pearly orange in color with a vitreous luster (Fig. 2). In thin section, garnet is colorless with a pink tint, high relief, and very few to no mineral inclusions.

The polished thin section of the mineral necessary for the chemical analysis was prepared in the laboratory of the Institute of Geosciences of the Federal University of Rio Grande do Sul (Brazil).

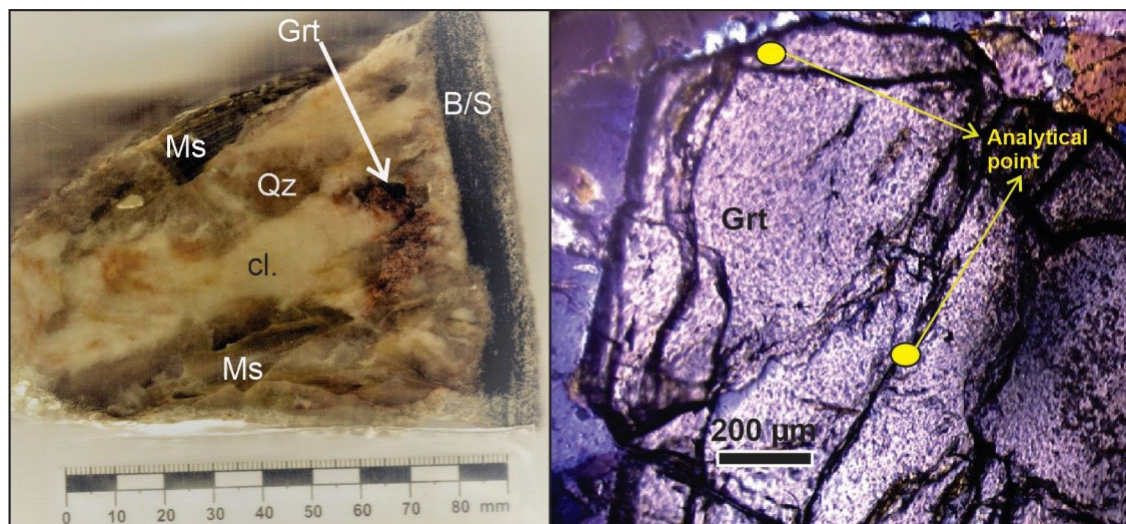


FIG. 2. The studied garnet from Rflejos de Mar pegmatite; left, photograph of hand specimen including host-rock of the pegmatite; right, photomicrographs of the graine 1 studied in this report, indicating the microanalysis points. **Grt**: garnet; **Ms**: muscovite; **Qz**: quartz; **cl.**: cleavelandite; **B/S**: banded schist.

At this same site, point analysis was carried out at the core and rim of four idiomorphic and sub-idiomorphic garnet grains using a CAMECA electron microprobe whose analytical conditions were an accelerating voltage of 15 keV, a probe current of 15nA and beam size of 5 µm. Albite was the standards used for Na; sanidine for Si, Al and K; diopside for Mg and Ca; hematite for Fe; rutile for Ti; chromium oxide for Cr and Rhodonite GEO MKII for Mn.

5. Results

The table 1 shows the chemical composition of the cores and rims of each of the four garnet crystals analyzed in this study. The compositional zoning stands out mainly in the divalent component in VIII-coordination (Fig. 3A, B) since the tetravalent cations in IV-coordination and trivalent cations in VI-coordination maintain nearly constant values both in the core and at the rim of the mineral. Thus, the average content of SiO₂ and Al₂O₃ in the cores of the grains is similar to that of the rims and corresponds to 36.4% and 20.6 wt%, respectively. Cr₂O₃ content is very low (avg. 0.03 wt%) and in most cases below detection level. The TiO₂ concentration has an average value in the core of 0.14 wt% while at the rim of the grains its value decreases to half that value (0.07 wt%). The figure

3B is a multi-element diagram showing graphically the compositional differences between core and rim of the grains expressed in wt%.

The component with the highest concentration corresponding to divalent cations is MnO in the analyzed sample, being variable between 34.07 and 35.39 wt% (avg. 34.5 wt%) in the core of the grains and between 28.25 and 30.77 wt% (avg. 29.31 wt%) at the rims. In terms of abundance within these cations, FeO follows in importance with values between 7.18 and 8.96 wt% (avg. 8.29 wt%) in the core of the grains and 11.78 and 13.75 wt% at the rims (avg. 12.95 wt%). The Fe/Mn ratio at the core of the grains is 0.24 while at the rims it is 0.44.

The average content of CaO and MgO in the core of the grains is 0.24 and 0.13 wt%, respectively, while at the rims it is 0.55 and 0.33 wt%.

There is a significant major elements compositional zoning (Table 1 and Fig. 3), which is characteristic in garnets for this kind of LCT pegmatitic systems. The minor components Ti and Cr, between the tetravalent cations in the tetrahedral position and the trivalent cation in the hexahedral position, vary from core to rim. However, the major divalent metals in the octahedral position, MnO and FeO, and the minor ones, MgO and CaO, also show notable changes in their concentrations from core to rim.

TABLE 1. CHEMICAL COMPOSITION OF MAJOR ELEMENTS OF THE GARNET FROM THE REFLEJOS DE MAR PEGMATITE, ANCASTI DISTRICT, PPP, ARGENTINA.

Sample	Grain 1 ◊		Grain 2 ◻		Grain 3 ◇		Grain 4 Δ	
	Core	Rim	Core	Rim	Core	Rim	Core	Rim
Oxides (wt%)								
SiO ₂	36.19	36.02	36.68	36.86	36.71	36.12	35.95	36.42
TiO ₂	0.11	0.16	0.13	0.04	0.17	0.05	0.16	0.04
Al ₂ O ₃	20.55	20.58	20.47	20.44	20.61	20.88	20.67	20.83
Cr ₂ O ₃	0.13	0.00	0.02	0.00	0.00	0.00	0.00	0.11
MgO	0.10	0.29	0.15	0.39	0.13	0.35	0.15	0.29
CaO	0.23	0.30	0.23	0.44	0.19	0.83	0.30	0.61
MnO	35.39	29.30	34.26	30.77	34.27	28.25	34.07	28.91
FeO	7.18	12.82	8.75	11.78	8.27	13.75	8.96	13.45
Total	99.88	99.47	100.69	100.72	100.35	100.23	100.26	100.66
Cation (wt%)								
Si	16.91	16.84	17.14	17.23	17.16	16.88	16.80	17.02
Ti	0.07	0.10	0.08	0.02	0.10	0.03	0.10	0.02
Al	10.88	10.89	10.84	10.82	10.91	11.05	10.94	11.02
Cr	0.09	0.00	0.01	0.00	0.00	0.00	0.00	0.08
Mg	0.06	0.17	0.09	0.24	0.08	0.21	0.09	0.18
Ca	0.17	0.21	0.17	0.31	0.14	0.59	0.22	0.44
Mn	27.41	22.69	26.54	23.83	26.54	21.88	26.39	22.39
Fe	5.58	9.96	6.80	9.16	6.43	10.69	6.97	10.46
Fe/Mn	0.20	0.44	0.26	0.38	0.24	0.49	0.26	0.47
apfu (base of 24 oxygens)								
Si	5.973	5.964	6.005	6.022	6.016	5.935	5.926	5.958
Ti	0.014	0.020	0.016	0.005	0.020	0.006	0.020	0.005
Total ^{IV}	5.987	5.984	6.021	6.027	6.036	5.941	5.946	5.963
Al	3.998	4.016	3.951	3.937	3.980	4.045	4.016	4.017
Cr	0.016	0.000	0.002	0.000	0.000	0.000	0.000	0.015
Total ^{VI}	4.014	4.016	3.953	3.937	3.980	4.045	4.016	4.032
Mg	0.025	0.071	0.036	0.096	0.033	0.085	0.037	0.072
Ca	0.041	0.053	0.041	0.076	0.034	0.146	0.053	0.107
Mn	4.948	4.109	4.752	4.259	4.756	3.932	4.757	4.007
Fe	0.991	1.775	1.199	1.610	1.134	1.889	1.236	1.841
Total ^{VIII}	6.005	6.008	6.028	6.041	5.957	6.052	6.083	6.027
Extreme member (mol. %)								
Prp	0.42	1.18	0.60	1.59	0.55	1.40	0.61	1.19
Grs	0.68	0.88	0.68	1.26	0.57	2.41	0.87	1.78
Sps	82.40	68.39	78.83	70.50	79.84	64.97	78.20	66.48
Alm	16.50	29.54	19.89	26.65	19.04	31.21	20.32	30.55

Components: **Prp**: Pyrope; **Grs**: Grossular; **Sps**: Spessartine, **Alm**: Almandine.

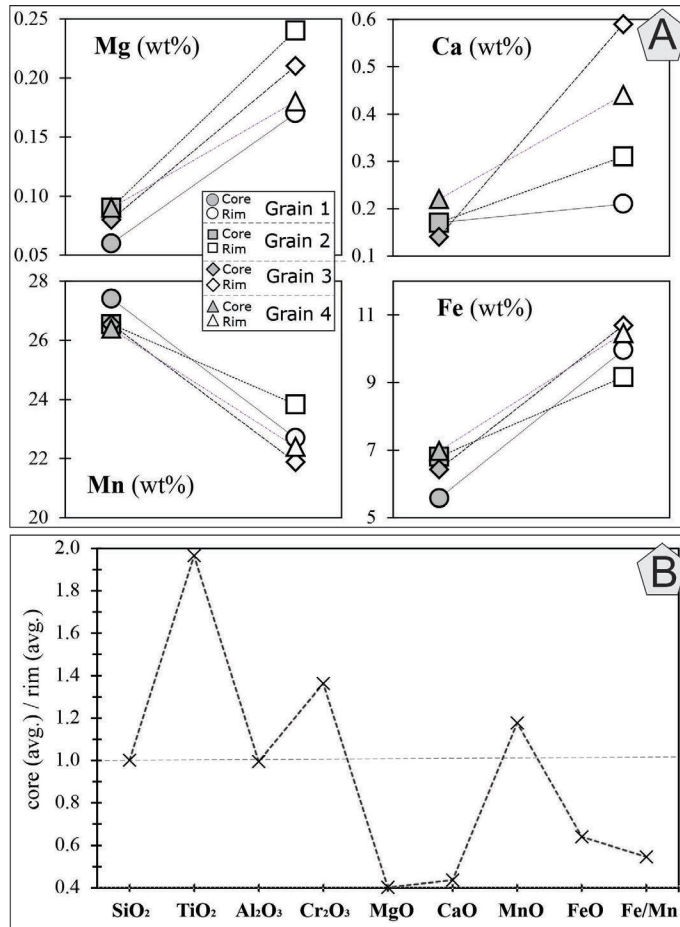
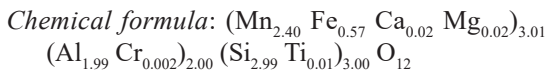


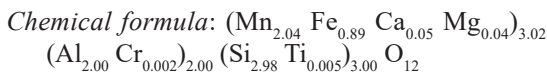
FIG. 3. **A.** Chemical compositional changes in the garnet from Reflejos de Mar pegmatite. **B.** Multi-element diagram displaying the average contents in the core and rim of the garnet.

In short, the core and rim of the analyzed garnet grains have a chemical and molecular formula that could be expressed as follows:

Core



Rim



Consequently, the Fe/Mn ratio and the amount of Mn (wt%) also shows the compositional zoning of the garnet of the Reflejos de Mar pegmatite (Fig. 4). The core and the rim of the crystals contain between 26.4 and 27.4 wt% Mn (avg. 26.7 wt%) and 21.9 and 23.8 wt% Mn (avg. 22.7 wt%), respectively, while the Fe/Mn ratio is between 0.20 and 0.26 (avg. 0.24) in the core of the crystal and between 0.38 and 0.49 (avg. 0.44) at the rim.

6. Discussion

Mn and Fe are the most abundant major divalent cations forming part of the spessartine and almandine component in the garnet of the outermost zones of the Reflejos de Mar pegmatite. The minor components Ca and Mg, contained in grossular and pyrope respectively,

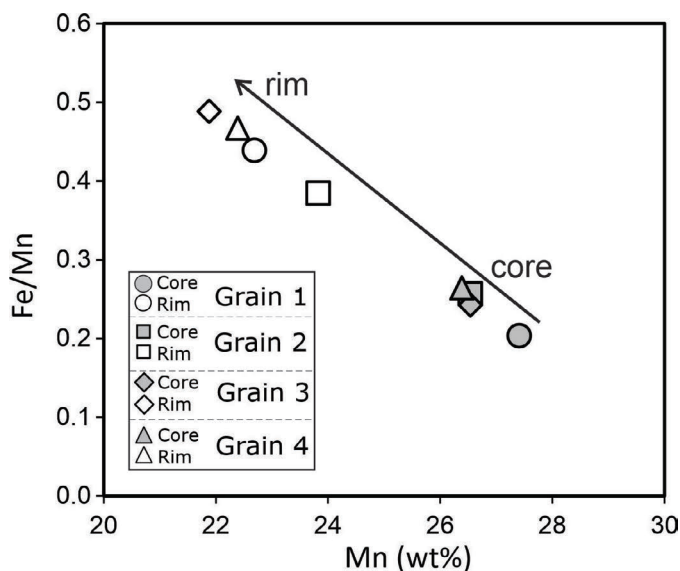


FIG. 4. Orthogonal diagram Fe/Mn versus Mn (wt%) for garnets of the Reflejos de Mar pegmatite, Sierra de Ancasti, Argentina.

are subordinated. This Mn-rich composition found in the studied garnet has been reported in several granitic pegmatites and also aplites distributed throughout the world (e.g., Černý *et al.*, 1985; London, 2008), most of which are highly evolved and frequently associated with Li mineralization belonging to the LCT pegmatite family (Fig. 5; Heimann *et al.*, 2012; Heimann, 2015; Moretz *et al.*, 2013; Nejbort *et al.*, 2018; Hernández-Filiberto *et al.*, 2021; Sousa *et al.*, 2021). The experimental studies by Maner *et al.* (2019) have suggested that an advanced fractional crystallization process (~95%) is necessary from the initial melt composition to achieve the formation of Mn-rich garnet, therefore, the spessartine composition is expected in highly fractionated granite-pegmatite systems in final stages of magmatism.

A Mn-rich core and the tendency to decrease towards the rim in individual garnet crystals of the Reflejos de Mar pegmatite, with the concomitant increase mainly of Fe in the same direction as crystallization proceeds, is a behavior similar to world numerous examples (Leake, 1967; Manning, 1983; Černý *et al.*, 1985; Nakano and Ishikawa, 1997; Yu *et al.*, 2021).

These variations in the composition of the magmatic garnets would be controlled by the composition of the original pegmatitic magma and the ability of the minerals that crystallize simultaneously with garnet to fractionate common elements from the melt (Černý *et al.*, 1985; Maner *et al.*, 2019; Hernández-Filiberto

et al., 2021), and also due to the difference in the growth rate of garnet (Nakano and Ishikawa, 1997).

For the case of the Reflejos de Mar pegmatite, the concomitant crystallization of garnet together with Fe-rich tourmaline (schorl), Mn-Fe bearing phosphates, minerals of the columbite-tantalite group, and subordinately apatite and muscovite may have influenced the garnet composition.

7. Conclusions

- The compositionally zoned garnet of the Reflejos de Mar LCT family Li-pegmatite from the Ancasti district has an average molecular constitution of $\text{Sps}_{79.8}\text{-Alm}_{18.9}$ in the core of the crystal and $\text{Sps}_{67.6}\text{-Alm}_{29.5}$ in the rim.
- The analyzed garnets show a composition compatible with garnets present in Li-bearing pegmatites, formed from a highly fractionated magma.
- Garnet composition can be used as an additional tool for exploration of Li-bearing pegmatites in the PPP.
- The compositional variations between core and rim in the individual grain would be linked to the original composition of the pegmatitic magma and regulated by the simultaneous co-precipitation with garnet of other mineral phases that would fractionate common elements of the melt.

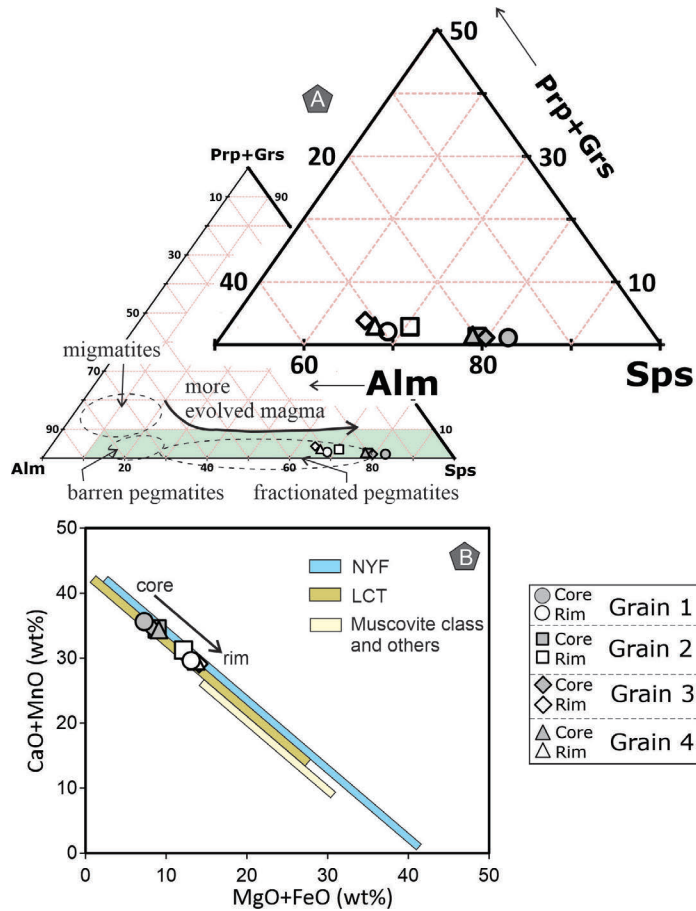


FIG. 5. **A.** Alm-(Prp+Grs)-Sps ternary diagram for the Reflejos de Mar pegmatite, on the left the complete diagram and to the right an enlargement of the Sps vertex. The composition of the analyzed garnets is dominated by the spessartine molecule and agrees with the composition of garnets formed from a magma with a high degree of fractionation. Fields for garnets from migmatites, barren and high differentiated pegmatites, and the arrow showing the sense of magmatic evolution are based on Hernández-Filiberto *et al.* (2021). The shaded area is 'pegmatite and granitic aplite' field extended by Sousa *et al.* (2021) from the originally of Remus *et al.* (2004). **Alm:** almandine; **Prp:** pyrope; **Grs:** grossular; **Sps:** spessartine. **B.** MgO+FeO versus CaO+MnO diagram to discriminate between different types of pegmatites (Modified from Moretz *et al.*, 2013 and Heimann, 2015). Garnets from the Reflejos de Mar pegmatite plot mostly in the fields of garnets associated with pegmatites of the LCT Family. LCT, Li-Cs-Ta pegmatite family; NYF, Nb-Y-F pegmatite family.

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References

- Aceñolaza, F.G.; Toselli, A.J. 1977. Esquema geológico de la Sierra de Ancasti, provincia de Catamarca. *Acta Geológica Lilloana* 14: 233-259.
- Aceñolaza, F.; Miller, H.; Toselli, A. 1983. La Geología de la Sierra de Ancasti. *Münster Forschung zur Geologie und Paläontologie*, Heft 59: 372 p. Münster.
- Alderton, D. 2020. Garnets. *Encyclopedia of Geology*, 2nd edition. Academic Press: 8 p. doi: <https://doi.org/10.1016/B978-0-08-102908-4.00172-7>.

- Černý, P.; Ercit, S. 2005. The classification of granitic pegmatites revisited. *The Canadian Mineralogist* 43: 2005-2026.
- Černý, P.; Meintzer, R.; Anderson, A. 1985. Extreme fractionation in rare-element granitic pegmatites: selected examples of data and mechanisms. *The Canadian Mineralogist* 23: 381-421.
- Cisterna, C. 2003. Faja intrusiva La Majada, Sierra de Ancasti, Catamarca: Caracterización petrológica-estructural. *Revista de la Asociación Geológica Argentina* 58 (1): 20-30.
- Dahlquist, J.; Alasino, P.; Galindo, C.; Casquet, C. 2006. Diferencias entre granates de rocas ígneas y metamórficas de edad famatiniana (Ordovícico), en las Sierras Pampeanas (Argentina). *MACLA* 6: 155-158.
- Dahlquist, J.; Rapela, C.; Baldo, E.; Murra, J.; Alasino, P.; Colombo, F. 2011. Stock monzogranítico El Chorro (Sierra de Ancasti, Catamarca): un ejemplo de magmatismo tipo S con granate ígneo. *Revista de la Asociación Geológica Argentina* 68: 195-204.
- Dahlquist, J.; Rapela, C.; Pankhurst, R.; Fanning, M.; Vervoort, J.; Hart, G.; Baldo, E.; Murra, J.; Alasino, P.; Colombo, F. 2012. Age and magmatic evolution of the Famatinian granitic rocks of Sierra de Ancasti, Sierras Pampeanas, NW Argentina. *Journal of South American Earth Science* 34: 10-25.
- Dahlquist, J.; Pankhurst, R.; Gasching, R.; Rapela, C.; Casquet, C.; Alasino, P.; Galindo, C.; Baldo, E. 2013. Hf and Nd isotopes in Early Ordovician to Early Carboniferous granites as monitors of crustal growth in the Proto-Andean margin of Gondwana. *Gondwana Research* 23: 1617-1630.
- Deer, W.A.; Howie, R.A.; Zussman, J. 1997. An Introduction to the Rock-Forming Minerals. Volume 1A. *The Geological Society*: 913 p.
- Fernández Lima, F.; Rinaldi, C.; Turazzini, G. 1972. Pegmatita litífera "Reflejos de Mar", Ancasti, provincia de Catamarca. *In Jornadas Geológicas Argentinas*, No. 4, Actas: 43-60.
- Galliski, M. 1994. La Provincia Pegmatítica Pampeana. I: Tipología y distribución de sus distritos económicos. *Revista de la Asociación Geológica Argentina* 49: 99-112.
- Galliski, M. 1999. Distrito pegmatítico Ancasti, Catamarca. *In Recursos minerales de la República Argentina* Zappetini, E.O.; editor). Instituto de Geología y Recursos Minerales, Servicio Geológico Minero Argentino: 393-396. Buenos Aires.
- Galliski, M. 2009. The Pampean Pegmatite Province, Argentina: a review. *Estudios Geológicos* 29 (2): 30-34.
- Galliski, M.; Márquez-Zavalía, M.F.; Roda-Robles, E.; Von Quadt, A. 2022. The Li-Bearing Pegmatites from the Pampean Pegmatite Province, Argentina: Metallogenesis and Resources. *Minerals* 12 (7). doi: <https://doi.org/10.3390/min12070841>
- Geiger, Ch.; Rossman, G. 2020. Micro- and nano-size hydrogarnet clusters and proton ordering in calcium silicate garnet: Part I. The quest to understand the nature of "water" in garnet continous. *American Mineralogist* 105: 455-467.
- Grew, E.; Lockock, A.; Mills, S.; Galuskina, I.; Galuskin, E.; Galenius, U. 2013. Nomenclature of the garnet supergroup. *American Mineralogist* 98 (4): 785-811.
- Hernández-Filiberto, L.; Roda-Robles, E.; Simmons, W.; Webber, K. 2021. Garnet as indicator of pegmatite evolution: the case study of pegmatites from the Oxford Pegmatite Field (Maine, USA). *Mineral* 11 (8). doi: <https://doi.org/10.3390/min11080802>
- Heimann, A. 2015. The chemical composition of gahnite and garnet as exploration guides to and indicators of rare element (Li) granitic pegmatites. U.S. Geological Survey, Open-File Report 1-24. United States.
- Heimann, A.; Bitner, J.; Wise, M.; Rodrigues Soares, D.; Mousinho Ferreira, A. 2012. The composition of garnet in granitic pegmatites. Geological Society of American Annual Meeting, Paper N° 87-6. Charlotte.
- Herrera, A. 1964. Las pegmatitas de la provincia de Catamarca. Estructura interna, mineralogía y génesis. *Revista de la Asociación Geológica Argentina* 19: 35-56.
- Javanmard, S.R.; Tahmasbi, Z.; Ding, X.; Khalaji, A.; Hetherington, C. 2018. Geochemistry of gamet in pegmatites from the Boroujerd Intrusive Complex, Sanandaj-Sirjan Zone, western Iran: implications for the origin of pegmatite melts. *Mineralogy and Petrology* 112: 837-856.
- Knüver, M. 1983. Dataciones radiométricas de rocas plutónicas y metamórficas. *In Geología de la Sierra de Ancasti* (Aceñolaza, F.; Miller, H.; Toselli, A.; editores). Münstersche Forschung zur Geologie und Paläontologie 59: 201-218.
- Laurs, B.M.; Knox, K. 2001. Spessartine garnet from Ramona, San Diego County, California. *Gems and Gemology* 37: 278-295.
- Leake, B. 1967. Zoned garnets from the Galway granite and its aplites. *Earth Planetary Sciences Letter* 3: 311-316.
- London, D. 2008. Pegmatites. *Mineralogical Association of Canada*: 347 p.
- Lottner, U. 1983. Las pegmatitas de la Sierra de Ancasti. *In Geología de la Sierra de Ancasti* (Aceñolaza, F.; Miller, H.; Toselli, A.; editores). Münstersche Forschung zur Geologie und Paläontologie 59:137-151.

- Maner, J.; London, D.; Icenhower, J. 2019. Enrichment of manganese to spessartine saturation in granite-pegmatite systems. *American Mineralogist* 104: 1625-1637.
- Mange, M.A.; Morton, A.C. 2007. Geochemistry of heavy minerals. In *Heavy Minerals in Use* (Mange, M.A.; Wright, D.T.; editors). *Developments in Sedimentology* 58, Elsevier: 345-391. Amsterdam.
- Manning, D.A. 1983. Chemical variation in garnets from aplites and pegmatites, peninsular Thailand. *Mineralogical Magazine* 47: 353-358.
- Marangone, S.; Sardi, F.; Altenberger, U.; Griffin, K.; Cisterna, C.; Schleicher, A. 2020. Geochemistry of the Villismán Granite, associated aplite-pegmatites and surrounding Li-pegmatites, Sierra de Ancasti, Argentina. *Journal of South American Earth Sciences* 103. doi: <https://doi.org/10.1016/j.jsames.2020.102764>
- Miller, H.; Willner, A. 1981. The Sierra de Ancasti (Catamarca Province), an example of polyphase deformation of Lower Paleozoic age in the Pampean Range. *Zbl. Geol. Paläont, Teil I* (3-4): 272-284.
- Miller, H.; Söllner, F. 2005. The Famatina complex (NW-Argentina): back-docking of an island arc or terrane accretion? Early Palaeozoic geodynamics at the western Gondwana margin. In *Terrane processes at the margins of Gondwana* (Vaughan, A.; Leat, P.; Pankhurst, R.; editors). *Geological Society of London, Special Publication* 246: 241-256. London.
- Moretz, L.; Heimann, A.; Bitner, J.; Wise, M.; Rodrigues Soares, D.; Mousinho Ferreira, A. 2013. The composition of garnet as indicator of rare metal (Li) mineralization in granitic pegmatites. In *International Symposium on Granitic Pegmatites*, No. 6, PEG2013- Abstracts: 94-95. New Hampshire.
- Muller, A.; Ihlen, P.; Larsen, R.; Spratt, J.; Seltnann, R. 2009. Quartz and garnet chemistry of South Norwegian pegmatites and its implications for pegmatite genesis. *Estudios Geológicos* 19 (2): 20-24.
- Nakano, T.; Ishikawa, Y. 1997. Chemical zoning of pegmatite garnets from the Ishikawa and Yamanoo areas, northeastern Japan. *Geochemical Journal* 31: 105-118.
- Nejbert, K.; Ilnicki, S.; Pieczka, A.; Szeleg, E.; Szuszkiewicz, A.; Turniak, K. 2018. Garnet from Juliana Pegmatite System, Sudetes - record of magmatic to hydrothermal evolution. In *Joint Central-European Mineralogical Conference*, No. 5, and *Mineral Sciences in the Carpathians Conference*, No. 7, Proceeding: 78. Banská Štiavnica.
- Pankhurst, R.J.; Rapela, C.W.; Fanning, C. 2000. Age and origin of coeval TTG, I- and S-type granites in the Famatinian belt of NW Argentina. *Transactions of the Royal Society of Edinburgh. Earth Sciences* 91: 151-168.
- Rapela, C.; Casquet, C.; Baldo, E.; Dahlquist, J.; Pankhurst, R.; Galindo, C.; Saavedra, J. 2001. La orogénesis del Paleozoico inferior en el margen proto-andino de América del Sur, Sierras Pampeanas, Argentina. *Journal of Iberian Geology* 27: 23-41.
- Remus, M.; De Ros, L.; Dillenburg, S.; Splendor, F.; Nunes, L.C. 2004. Aplicação da microsonda eletrônica na análise de proveniência: Granodas - tracadores de áreas-fonte nas Bacias de Santos e Pelotas. *Boletim Dez Anos de Microsonda em Porto Alegre*: 101-107.
- Rossi, J.; Willner, A.; Toselli, A. 2002. Ordovician metamorphism of the Sierras Pampeanas, Sistema de Famatina and Cordillera Oriental, Northwestern Argentina. *Serie de Correlación Geológica* 16: 225-242.
- Rzyziuk, J.; Sardi, F.; Báez, M.; Fogliata, A.; Hagemann, S. 2014. Petrografía y geoquímica de los granitos asociados a manifestaciones de fluorita en la zona de El Alto, Sierra de Ancasti, provincia de Catamarca. *Acta Geológica Lilloana* 26 (2): 95-110.
- Sami, M.; Ntaflos, T.; Mohamed, H.; Farahat, E.; Hauzenberger, Ch.; Mahdy, N.; Abdelfadil, K.; Fathy, D. 2020. Origin and petrogenetic implications of spessartine garnet in highly-fractionated granite from the Central Eastern Desert of Egypt. *Acta Geologica Sinica (English Edition)* 94 (3): 763-776.
- Sardi, F.G.; Aliaga Pueyrredón, J.M.; Toledo Ceccarelli, J.D. 2013. Estudio geológico preliminar de las pegmatitas litíferas de los grupos Villismán y El Taco, Sierra de Ancasti, Catamarca. *Acta Geológica Lilloana* 25 (1-2): 69-73.
- Sardi, F.; Marangone, S.; Demartis, M.; Altenberger, U. 2017. Pegmatitas litíferas del Grupo Villismán, Distrito Ancasti, Catamarca. I.- Rasgos petrográficos y geoquímicos. II.- Textura de la mena y preliminar estimación de su potencialidad minera. In *Congreso Geológico Argentino*, No. 20, Simposio 2: *Geología endógena y exógena del litio en Argentina*, Actas: 26-37. San Miguel de Tucumán.
- Sokolov, Y.; Khlestov, V. 1990. Garnets as indicators of the physicochemical conditions of pegmatite formation. *International Geology Review* 32: 1095-1107.
- Sousa, S.; Ávila, C.; Neumann, R.; Leite Faulstich, F.; Alves, F.; Cidade, T.; da Silva, V. 2021. Mineral chemistry and genetic implications of garnet from the São João del Rei Pegmatitic Province, Minas Gerais, Brazil. *Brazilian Journal of Geology* 51 (1). doi: <https://doi.org/10.1590/2317-488920210190136>
- Toselli, A.J.; Reissinger, F.; Durand, F.; Bazán, C. 1983. Rocas graníticas. In *Geología de la Sierra de Ancasti* (Aceñolaza, F.; Miller, H.; Toselli, A.; editores). *Münstersche Forschung zur Geologie und Paläontologie* 59: 79-99.

- Toselli, A.J.; Aceñolaza, F.; Rossi de Toselli, J. 1986. A proposal for the systematization of the Upper Precambrian-Lower Paleozoic basement in the Sierras Pampeanas, Argentina. *Zentralblatt für Geologie und Paläontologie*, Teil I: 1227-1233.
- Toselli, A.J.; Miller, H.; Aceñolaza, F.; Rossi, J.; Söllner, F. 2007. The Sierra de Velasco (northwestern Argentina)-an example for polyphase magmatism at the margin of Gondwana. *Neues Jahrbuch für Geologie und Paläontologie* 246 (3): 325-345.
- Toselli, A.J.; Rossi, J.A.; Basei, M.A.; Passarelli, C.R. 2011. Petrogenesis of Paleozoic post-collisional peraluminous leucogranites, Sierra de Ancasti, northwest Argentina. *Neues Jahrbuch für Geologie und Paläontologie Abhandlungen* 261 (2): 151-164. doi: <https://doi.org/10.1127/0077-7749/2011/0152>
- Willner, A. 1983. Evolución metamórfica. In *Geología de la Sierra de Ancasti* (Aceñolaza, F.; Miller, H.; Toselli, A.; editores). *Münstersche Forschung zur Geologie und Paläontologie* 59:189-200.
- Yu, M.; Xia, Q.; Zheng, Y.; Zhao, Z.; Chen, Y.; Chen, R.; Luo, X.; Li, W.; Xu, H. 2021. The composition of garnet in granite and pegmatite from the Gangdese orogen in southeastern Tibet: Constraints on pegmatite petrogenesis. *American Mineralogist* 106: 265-281.