

## THE COMPOSITION OF GAHNITE IN GRANITIC PEGMATITES FROM THE PAMPEAN PEGMATITE PROVINCE, ARGENTINA: IMPLICATIONS FOR PEGMATITE FRACTIONATION

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### ABSTRACT

Gahnite from LCT granitic pegmatites of the Comechingones (Blanca Dora, Juan Román, Magdalena, La Ona, and Sin Nombre pegmatites) and Conlara (Nancy pegmatite) pegmatite districts, Argentina, was analyzed to investigate the relationship between its chemistry, pegmatite mineralogy, and pegmatite melt evolution. Based on the molecular proportions of endmembers (gahnite, hercynite, spinel, and galaxite) the composition of gahnite in these pegmatites is defined by the ranges  $\text{Ghn}_{77.7-91.0}\text{Hc}_{7.4-20.0}\text{Spl}_{0.25-3.37}\text{Glx}_{0.7-2.4}$ , which fall within the previously defined field for granitic pegmatites. Gahnite from the Nancy pegmatite has higher Mg and Mn contents than gahnite from the pegmatites of the Comechingones pegmatite district. Chemical variation within gahnite crystals is characterized by higher Zn (~2.8 wt.% ZnO) and lower Fe (~2.6 wt.% FeO) contents near the edge compared to inner portions, reflecting the evolution of the pegmatite melt *via* simple fractional crystallization. Other crystals show a complex zoning pattern of oscillations in Fe and Zn contents within the crystal and higher Zn and lower Fe near the rim compared to the core. A plot of molecular  $\text{Fe}^{2+} + \text{Mg}$  versus Zn + Mn yields a strong negative correlation and best displays the substitutions within the gahnite crystal structure and is the best to determine relative pegmatite melt evolution. Without implying a co-magmatic origin of the pegmatites, based on pegmatite mineralogy, Zn contents, Zn/Fe<sup>2+</sup> ratios, and coupled Fe<sup>2+</sup>+Mg and Zn+Mn values in gahnite, the relative degree of evolution of the pegmatites increases in the order: Sin Nombre → Magdalena → Juan Román → Blanca Dora → Nancy → La Ona. Based on the composition of gahnite in worldwide granitic pegmatites reported in the literature and those obtained here, the composition of gahnite in these rocks is defined by the endmember ranges  $\text{Ghn}_{50-98}\text{Hc}_{1-50}\text{Spl}_{0-7}$ . This study shows that the major element composition of gahnite in granitic pegmatites can effectively be used to determine the relative degree of evolution of pegmatite-forming melts.

*Keywords:* gahnite, Zn, granitic pegmatites, melt evolution, chemistry, Pampean Pegmatite Province, Argentina.

### INTRODUCTION

Zinc-rich spinel ( $[\text{Zn,Fe,Mg}]\text{Al}_2\text{O}_4$ ), the zinc-rich member of the spinel group of minerals, is an accessory mineral in aluminous metasedimentary rocks, metabauxites, skarns, marbles, banded iron formations, metamorphosed massive sulfide deposits (MMSDs), quartz veins, granitoids, and granitic pegmatites (*e.g.*, Spry & Scott 1986a, Heimann *et al.* 2005, O'Brien *et al.* 2014). Gahnite, the Zn endmember of the group, has been reported in granitic pegmatites, most commonly in metasomatic replacement

bodies, fracture fillings, and intermediate zones (*e.g.*, Černý & Hawthorne 1982, Soares *et al.* 2007). However, the compositional variations of gahnite have so far only been investigated in two pegmatite districts to understand the relative evolution of the pegmatite melts (*e.g.*, Batchelor & Kinnaird 1984, Soares *et al.* 2007).

Gahnite occurs as an accessory mineral in the LCT (lithium, cesium, tantalum) family, rare-element class, beryl-columbite-phosphate subtype, and muscovite-rare element class Li subclass granitic pegmatites (based on the Černý & Ercit 2005 and Černý

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*et al.* 2012 classification) of the Comechingones and Conlara pegmatite districts of the large Pampean Pegmatite Province, Argentina (Galliski 1994a). The Comechingones and Conlara pegmatite districts are economically important and have produced large amounts of beryl, mica, K-feldspar, quartz, Ta ore minerals, Li minerals, and Bi minerals since 1930 (Galliski & Černý 2006, Galliski 2009). However, chemical studies of gahnite from this important pegmatite province have not been undertaken. With the exception of two detailed studies, one of columbite-tantalite from several pegmatites in the province (Galliski & Černý 2006) and one of bobfergusonite from the Nancy pegmatite (Tait *et al.* 2004), chemical analyses of other minerals from the pegmatites that are the subject of this study have not previously been performed.

In this study we present the major element composition of gahnite from six granitic pegmatites from the Comechingones (Blanca Dora, Juan Román, Magdalena, La Ona, and Sin Nombre pegmatites) and Conlara (Nancy pegmatite) pegmatite districts of the Pampean Pegmatite Province. The objective of this study is to determine the compositional variations of gahnite in these pegmatites at the scale of the pegmatite district, single pegmatite bodies, and within individual crystals to ultimately understand the significance of the variations for pegmatite melt fractionation. In the context of the pegmatite's mineralogy and the composition of gahnite in granitic pegmatites worldwide, the composition of gahnite from the studied pegmatites is used to advance our understanding of the chemical characteristics and relative evolution of the magmatic-hydrothermal melts that led to the formation of the various pegmatites. Available compositions of pegmatite-derived gahnite are then used to re-define the compositional field of gahnite in granitic pegmatites. A comparison between the composition of gahnite in granitic pegmatites and that in MMSDs, where it is most abundant, is presented at the end.

#### SAMPLING AND ANALYTICAL METHODS

Samples of gahnite were collected from granitic pegmatites from the Comechingones (Blanca Dora, Juan Román, Magdalena, La Ona, and Sin Nombre pegmatites) and Conlara (Nancy pegmatite) pegmatite districts in the Córdoba and San Luis Provinces of central and northwestern Argentina. Polished thick sections (200  $\mu\text{m}$ ) were made from mineral separates and larger specimens of granitic pegmatite samples collected in the field. Petrographic analysis was conducted using Olympus BX51 and BX43 dual reflected/transmitted light microscopes housed in the Department of Geological Sciences at East Carolina University (ECU) to determine the mineralogy and identify areas for further analysis based on the characteristics of each gahnite sample (*e.g.*, crystal size,

shape, and the presence of inclusions). An FEI Quanta 200 Mark 1 variable-pressure scanning electron microscope (SEM) interfaced with an Oxford INCA X-act X-ray energy dispersive spectroscopy (EDS) elemental detector housed in the Department of Biology at ECU was used to obtain images, a qualitative estimate of the composition of unknown minerals, and elemental mapping. Operating conditions for imaging under high vacuum (0.45 torr) were an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 4.5  $\mu\text{m}$ . Copper was used for standardization and EDS analysis was done under 20 kV using a beam diameter of 6  $\mu\text{m}$ .

Electron microprobe (EMP) analysis was conducted at Fayetteville State University, NC, using a JEOL JXA 8530F Hyperprobe electron microprobe. Operating conditions were an accelerating voltage of 20 kV, a beam current of 10 nA, and beam diameters of 3 and 10 micrometers. Standards used for these analyses included Astimex almandine garnet (Si, Mg, Fe), bustamite (Ca, Mn), sanidine (K), synthetic chromium oxide (Cr), synthetic rutile (Ti), and Smithsonian gahnite (Al, Zn). Transects and individual spot analyses were conducted to check for core-to-rim variations. A total of 239 analyses were obtained from 10 crystals (Table A1, Electronic Appendix, available from the MAC Depository of Unpublished Data, document gahnite CM53-6\_10.3749/canmin.1400100).

Gahnite endmembers and ferric iron were calculated assuming an ideal spinel formula (*i.e.*,  $[\text{Mg,Fe,Zn,Mn}]\text{Al}_2\text{O}_4$ ) and calculating atoms per formula unit (*apfu*) for 3 cations and normalized to 4 oxygen atoms, following this method: (1) the amount of  $\text{Fe}^{2+}$  was calculated by stoichiometry, and the amount of  $\text{Fe}^{2+}$  by subtraction of  $\text{Fe}^{3+}$  from total Fe; (2) the amount of  $\text{Fe}^{2+}$  for the magnetite endmember was calculated by dividing the number of  $\text{Fe}^{3+}$  from (1) by 2; (3) the total amount of Fe in magnetite was calculated by adding (1) and (2); (4) the amount of Fe for hercynite was calculated by subtracting the amount of Fe for magnetite from the total amount of Fe; (5) the amount of Mn for galaxite, Mg for spinel, and Zn for gahnite are the calculated numbers of *apfu*; (6) the mol.% of each spinel endmember was calculated by normalizing the values obtained for each endmember by their sum.

#### GEOLOGIC SETTING

The Pampean Pegmatite Province, Argentina, is one of the largest pegmatite provinces in South America with an approximate area of  $\sim 800$  km by  $\sim 200$  km (Galliski 1994b, Galliski & Černý 2006). The development of the province took place from the Neoproterozoic to the Paleozoic during two main orogenic cycles, the Pampean ( $\sim 550$  Ma to  $\sim 510$  Ma) and Famatinian ( $\sim 500$  Ma to  $\sim 435$  Ma) (Sims *et al.* 1998, Schwartz *et al.* 2008, Galliski 2009, Demartis *et al.* 2010, Drobe *et al.* 2011). Pegmatites formed in

the province during three main periods: the Pampean orogeny, early in the Famatinian orogeny, and post-Famatinian orogeny (Galliski & Linares 1999, Otamendi *et al.* 2004, Galliski & Černý 2006). These events resulted in pegmatites of the rare-element and muscovite-rare-element classes of the LCT family, and muscovite class (Galliski *et al.* 2011) (based on the classification scheme of Černý & Ercit 2005 and Černý *et al.* 2012). Several of the pegmatites are economically important and they have produced 25,000 tonnes (t) of beryl, 45 t of Ta ore minerals, 1,000 t of Li-bearing minerals, 20 t of bismuth minerals, 40,000 t of mica, 500,000 t of K-feldspar, and 500,000 t of quartz since 1930 (Galliski & Černý 2006, Galliski 2009).

The Pampean- and Famatinian-age pegmatites have been divided into districts and include, from north to south, the Centenario, Cerro Blanco, El Quemado, Quilmes, Calchaquí, Ambato, Ancasti, Sierra Brava, Velasco, Valle Fértil, Alta Gracia, Punilla, Comechingones, Altautina, La Estanzuela, Conlara, and Totoral districts (Galliski 1994a, Galliski & Černý 2006, Schwartz *et al.* 2008, Galliski 2009, Galliski *et al.* 2011, Galliski & Sfragulla 2014). The studied gahnite is derived from pegmatites that are part of the Conlara and Comechingones pegmatite districts, as defined and characterized by Galliski (1994a, 1999a, b), in the eastern Sierras Pampeanas located between the Archean-Paleoproterozoic Río de la Plata craton to the east and the Grenville Cuyania-Precordillera terrane to the west (Siegesmund *et al.* 2010). Below we describe the two pegmatite districts, including location, origin, and host rocks, as well as the individual pegmatites. A summary of the characteristics of the pegmatites is presented in Table 1.

#### *Conlara Pegmatite District*

The Conlara pegmatite district is located in the northern portion of the Sierras de San Luis (Fig. 1; Galliski 1999b, Galliski *et al.* 2011). Pegmatites of this district possibly formed by fractionation of S-type granitic melts derived from partial melting of the Puncoviscana Formation during the Famatinian orogenic event (Galliski 1999b, 2009, Galliski *et al.* 2011, Drobe *et al.* 2011). This formation varies from very-low grade to low grade metasedimentary rocks in the northern region to medium-to-high metamorphic grade gneisses and migmatites towards the southern region (Zimmerman 2005, Galliski 2009, Drobe *et al.* 2011, Adams *et al.* 2011). The pegmatite melts intruded into crystalline basement rocks dominated by the Abukuma-type metamorphic belt locally forming the Conlara Metamorphic Complex (Sims *et al.* 1998, Galliski 1999b). The closest granitic body, the El Peñón granite, is an S-type granite that crops out ~3,500 m west of the Nancy pegmatite (Steenken *et al.* 2005) and could represent the parental granite of the pegmatite.

Many pegmatites in the district have been classified into different groups based on geographic location (Galliski 1999b). Pegmatites located at the southern end of the district are classified as beryl-rich granitic pegmatites and pegmatites in the north and northwest are lithium-rich pegmatites (Galliski 1999b). The general mineralogy of the pegmatites in the province includes K-feldspar, albite, quartz, and muscovite, accessory spodumene, amblygonite [(LiAl(PO<sub>4</sub>)(F))], beryl, columbite-group minerals [(Mn,Fe)(Nb,Ta)<sub>2</sub>O<sub>6</sub>], and gahnite, and rare lithiophilite (LiMnPO<sub>4</sub>) and bismuthinite (Bi<sub>2</sub>S<sub>3</sub>) (Galliski 1999b). Several pegmatites of the district have alteration zones (*e.g.*, tourmalinization, muscovitization, and silicification) that generally reach several centimeters into the country rocks (Galliski 1999b).

*Nancy Pegmatite.* The Nancy pegmatite is a moderately evolved LCT family, rare-element class, beryl-columbite-phosphate subtype pegmatite that intruded into medium-grade gray gneisses of the Conlara Metamorphic Complex (448–420 Ma) (Sims *et al.* 1998, Steenken *et al.* 2004, 2006, 2008, 2010). It has a tabular shape, is discordant, its width varies from 4 m in the south to 28 m in the north, and it is exposed for 140 m (Tait *et al.* 2004). Well-defined internal zonation consists of border, wall, and intermediate zones, and a quartz core. A 2–3 mm thick muscovite layer is present along the contact with the host rock and a similar layer divides the border and wall zones. The wall zone is generally 10 cm thick and contains K-feldspar, fine-grained quartz, and minor albite and muscovite. The intermediate zone is separated from the wall zone by a massive milky quartz layer and consists of K-feldspar, albite, quartz, muscovite, gahnite, beryl, and columbite. Gahnite occurs as isolated crystals surrounded by fine-grained quartz, feldspar, and muscovite. The K-feldspar is partially albitized and intergrown with coarse-grained quartz and 10 cm wide muscovite books. Tait *et al.* (2004) also described garnet as a common accessory mineral residing as inclusions within K-feldspar and albite in the intermediate zone. Minor, interstitial, fine-grained tourmaline was recently found. The quartz core is not continuous throughout the pegmatite body and, where present, is composed of coarse-grained milky quartz. Phosphate nodules (up to 50 × 30 × 20 cm), found throughout the pegmatite, consist of very dark green to black Mg-Ca-bearing bobfergusonite [Na<sub>2</sub>Mn<sub>5</sub>FeAl(PO<sub>4</sub>)<sub>6</sub>], Mn-rich apatite and Mn-rich wyllieite [(Na,Ca,Mn)(Mn,Fe)(Fe,Mg)Al(PO<sub>4</sub>)<sub>3</sub>], minor quartz, sphalerite, and pyrite, and secondary limonite and hematite (Tait *et al.* 2004).

*Pegmatites of the Comechingones Pegmatite District.* The Comechingones pegmatite district has an approximate area of 800 km<sup>2</sup> (Demartis *et al.* 2010) and is located in the northern end of the Sierra de los Comechingones of the Sierras de Córdoba, Argentina (Fig. 1; Galliski 1999a, Drobe *et al.* 2011, Siegesmund *et al.* 2010, Morteani *et al.* 2012).

TABLE 1. CHARACTERISTICS OF GAHNITE-BEARING PEGMATITES FROM THE CONLARA AND COMECHINGONES PEGMATITE DISTRICTS, PAMPEAN PEGMATITE PROVINCE, ARGENTINA

Pegmatite	Blanca Dora	Juan Román	La Ona	Magdalena	Sin Nombre	Nancy
District	Comechingones	Comechingones	Comechingones	Comechingones	Comechingones	Conlara
Group	Co. de Agustín	Co. Las Ovejas	Co. Las Ovejas	Co. Redondo	Co. de Agustín	Villa Praga-Las Lagunas
Thickness (m)	5	20	-	5 – <40	30	4 – 28
Length (m)	300	240	1000	200	209	>140
Shape	Tabular	Tabular	Tabular	Tabular	Tabular	Tabular
Orientation	Concordant	Concordant	Concordant	Subhorizontal	Discordant	Discordant
Host Rock	Augen-gneiss	Augen-gneiss	Augen-gneiss	Cordierite migmatite	Augen-gneiss	Medium-grade grey gneiss
Formation	Guacha Corral Shear Zone	Guacha Corral Shear Zone	Guacha Corral Shear Zone	Guacha Corral Shear Zone	Guacha Corral Shear Zone	Conlara Metamorphic Complex
Classification	REL-Li – beryl-columbite-phosphate sub-type (LCT)	REL-Li – beryl-columbite-phosphate sub-type (LCT)	REL-Li – beryl-columbite-phosphate sub-type (LCT)	REL-Li – beryl-columbite-phosphate subtype (LCT)	MS-REL – Li (LCT)	REL-Li – beryl-columbite-phosphate sub-type (LCT)
Mineralogy	Qz, Kfs, Ab, Ms, Grt, Brl, Ghn, Fap, Col	Qz, Kfs, Ab, Ms, Grt, Brl, Ghn, Fap, Col	Qz, Kfs, Ab, Ms, Grt, Brl, Ghn, Col, U minerals, Phos	Qz, Kfs, Ab, Ms, Grt, Brl, Ghn, Fap, Col, Trp	Qz, Kfs, Ab, Ms, Grt, Brl, Ghn, Tur, Aut, Ap, Hem <sup>1</sup>	Qz, Kfs, Ab, Ms, Grt, Brl, Ap, Ghn, Col, Tti, Py, Sp, Bfg, Wyl, Hem <sup>1</sup> , Lm <sup>1</sup>
Rare-metals	Be, Nb	Be, Nb	Be, Nb, U	Be, Nb	Be	Be, Nb
Age (Ma)	466 – 530	466 – 530	466 – 530	466 – 530	466 – 530	435 – 500
References	3, 4, 5	3, 4, 5	3, 4, 5	3, 4, 5, 6	3, 4, 5, 7	1, 2

Mineral abbreviations (\* Denotes those from Whitney & Evans 2010): Ab\* – Albite, Ap\* – Apatite, Aut\* – Autunite, Bri\* – Beryl, Bfg – Bobfergusonite, Col – Columbite, Fap – Fluorapatite, Ghn\* – Gahnite, Grt\* – Garnet, Hem<sup>1</sup> – Hematite, Kfs\* – K-feldspar, Lm\* – Limonite, Ms\* – Muscovite, Phos – Phosphates, Py\* – Pyrite, Qz\* – Quartz, Sp\* – Sphalerite, Tti – Triplite, Trp – Tourmaline, Wyl – Wylite. Secondary References as follows: 1 Galliski (1999b), 2 Tait *et al.* (2004), 3 Hub (1994), 4 Galliski (1999a), 5 Galliski & Sfragulla (2014), 6 Galliski & Černý (2006), 7 Rinaldi (1968). REL-Li refers to rare-element class, Li subclass pegmatites; MS-REL refers to muscovite-rare element class pegmatites.

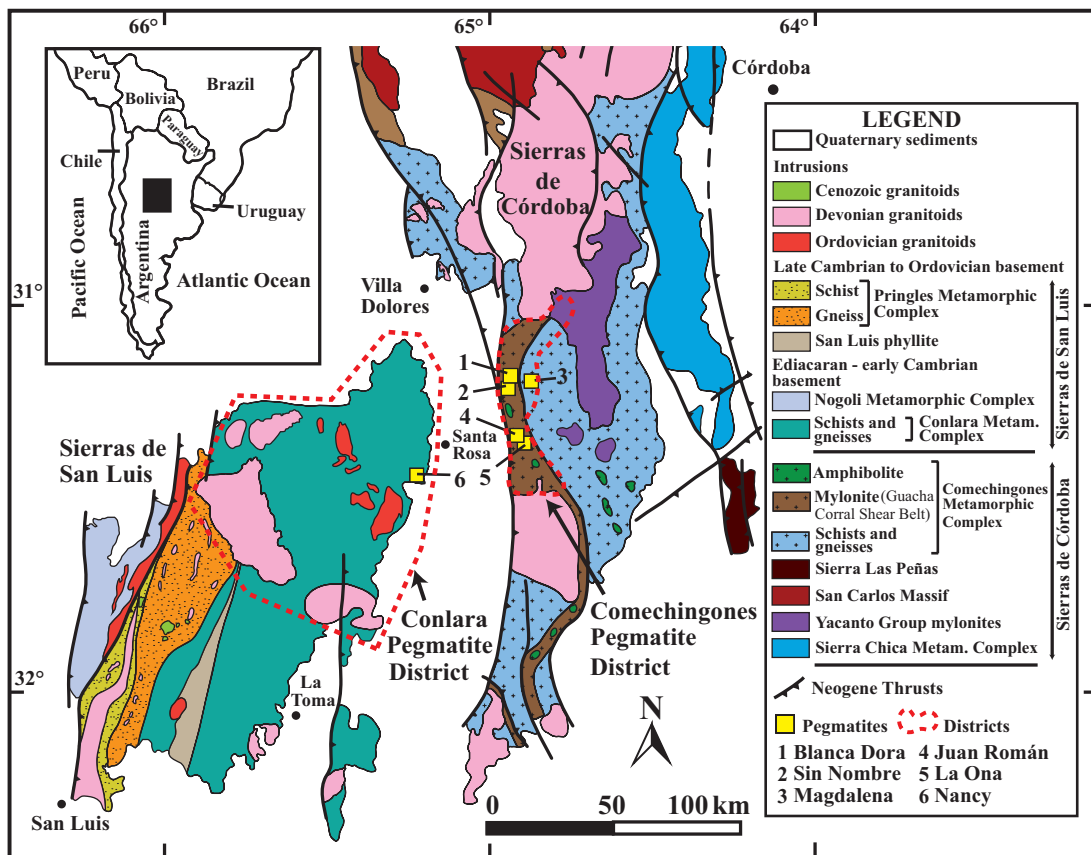


FIG. 1. General geologic map showing the location of the Comechingones and Conlara pegmatite districts in the Pampean Pegmatite Province, Argentina. Modified from Steenken *et al.* (2010), von Gosen & Prozzi (1998), and Galliski & Sfragulla (2014). The numbers refer to the following pegmatites: 1 Blanca Dora, 2 Sin Nombre, 3 Magdalena, 4 Juan Román, 5 La Ona, 6 Nancy.

Granitic pegmatites of the district formed by extreme magmatic differentiation of S(+I)-type granitic melts and were emplaced in basement gneisses, amphibolites, cordieritic migmatites, limestones, and scarce serpentinites formed during the Pampean orogeny (~580 Ma to ~510 Ma) (Sims *et al.* 1998, Galliski 1999b, 2009, Galliski & Černý 2006, Demartis *et al.* 2011, Drobe *et al.* 2011, Galliski & Sfragulla 2014). The Sin Nombre, Juan Román, La Ona, and Blanca Dora pegmatites intruded into augen-gneisses whereas the Magdalena pegmatite intruded into cordierite migmatites (Galliski & Černý 2006).

The pegmatites are tabular in shape, range in thickness from 5 to 40 m, and are concordant to slightly discordant, except for the Magdalena pegmatite which is subhorizontal (Galliski & Sfragulla 2014). They range in length from 200 m (Magdalena) to 1,000 m (La Ona). The lengths of the remaining pegmatites are intermediate (209 m for Sin Nombre, 240 m for Juan Román, and 300 m for Blanca Dora). Commonly well-

developed zonation includes border, wall, intermediate, and quartz core zones, and minor replacement bodies (Galliski 1999a, Galliski & Sfragulla 2014). Albite, K-feldspar, quartz, and muscovite, with accessory beryl, tourmaline, garnet, columbite, apatite, uraninite, triplite, gahnite, allanite, epidote, pyrite, and chalcocopyrite comprise the general mineralogy of the Comechingones pegmatites (Galliski 1999a, Galliski & Černý 2006, Galliski & Sfragulla 2014). Secondary uranium-lead minerals masuyite  $[\text{Pb}(\text{UO}_2)_3\text{O}_3(\text{OH})_2 \cdot 3(\text{H}_2\text{O})]$ , fourmarierite  $[\text{Pb}_{1-x}\text{O}_{3-2x}(\text{UO}_2)_4(\text{OH})_{4+2x} \cdot 4\text{H}_2\text{O}]$ , and vandendriesscheite  $[\text{Pb}_{1.6}(\text{UO}_2)_{10}\text{O}_6(\text{OH})_{11} \cdot 11(\text{H}_2\text{O})]$ , uranium-phosphate minerals autunite  $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10-12(\text{H}_2\text{O})]$  and meta-autunite  $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2-6(\text{H}_2\text{O})]$ , uranophane  $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}]$ , malachite, pyrolusite ( $\text{MnO}_2$ ), and phosphosiderite  $[\text{Fe}^{3+}(\text{PO}_4) \cdot 2\text{H}_2\text{O}]$  have been identified within granitic pegmatites of the district (Rinaldi 1968). The majority of the accessory minerals are concentrated in the core edges and intermediate zones of the pegmatites.

Gahnite is located in the core edges partially replaced or covered with muscovite.

Based on mineralogy, the studied pegmatites belong to the LCT family and are divided into two classes, the rare-element class beryl-columbite-phosphate subtype and the muscovite-rare element class Li subclass (Table 1; Hub 1994, 1995, Galliski 1999a, 2009, Demartis *et al.* 2012). Many of the pegmatites have been exploited for beryl, muscovite, columbite, and uranium and have significant reserves of beryl, muscovite, feldspar, and quartz (Galliski 1999a, 2009). The Magdalena pegmatite is one of the most exploited for the production of beryl in the Comechingones pegmatite district (Galliski 1999a). Defined based on mineralogy, the geochemical evolution of the pegmatites

ranges from the poorly evolved Sin Nombre pegmatite that contains apatite and beryl but lacks columbite-group minerals, to the most evolved La Ona pegmatite, which has beryl, columbite-group minerals, phosphates, and uranium minerals (Table 1; Hub 1994, Galliski & Černý 2006, Galliski & Sfragulla 2014).

#### CHARACTERISTICS OF GAHNITE

In the studied pegmatites gahnite occurs as 'emerald' green to slightly bluish-green crystals ranging in size from 0.2 to 20 mm and commonly associated with muscovite and less frequently with quartz and microcline (Fig. 2). The contacts between gahnite, quartz, and feldspar are sharp and do not display alteration or reaction.

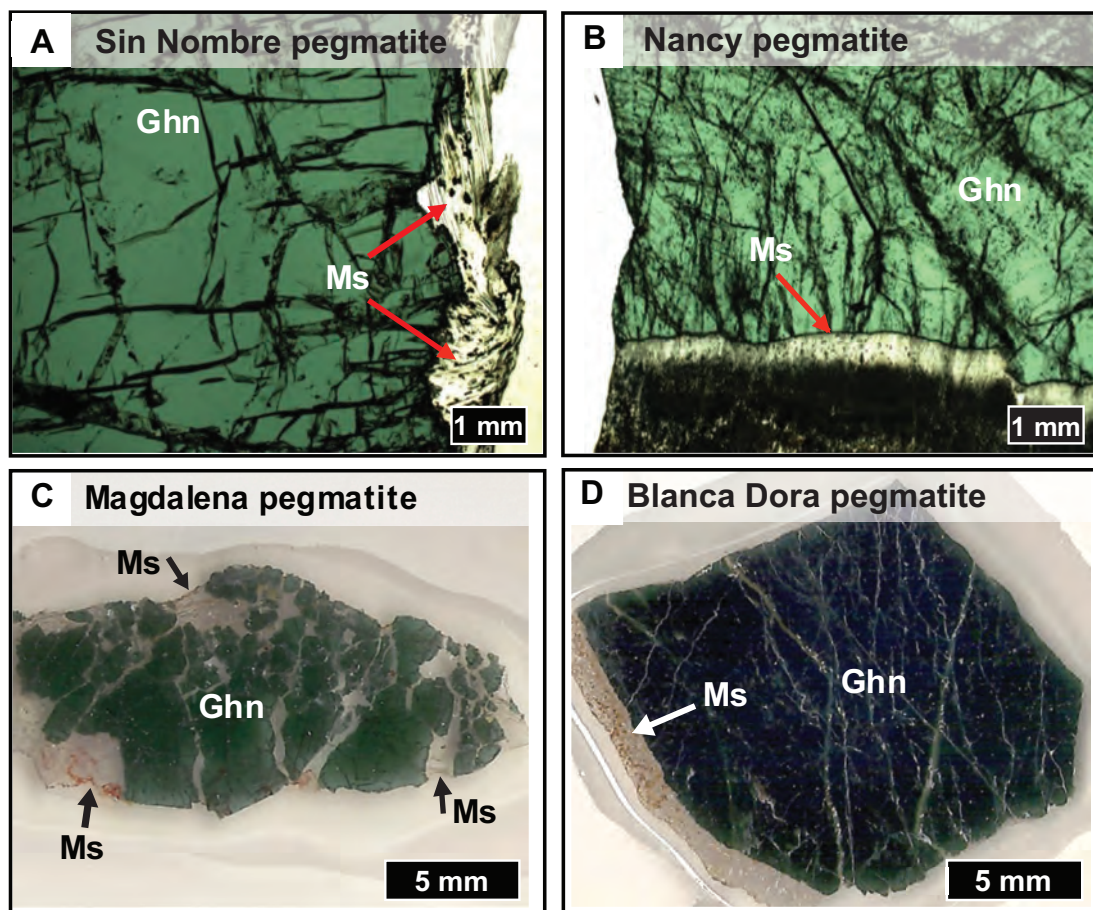


FIG. 2. Plane-polarized transmitted-light photomicrographs and scans of gahnite (Ghn) from granitic pegmatites of the Comechingones and Conlara pegmatite districts of central and northwestern Argentina. (A) Green gahnite crystal with fractures next to muscovite (Ms). Plane polarized light. Sin Nombre pegmatite, sample GH274A. (B) Green gahnite crystal with fractures and tiny inclusions in contact with muscovite. Plane polarized light. Nancy pegmatite, sample NA001. (C) Green, brecciated gahnite crystal with pale rims and muscovite filling fractures. Scanned polished thick-section. Magdalena pegmatite, sample GH272. (D) Dark green gahnite crystal, in contact with muscovite, showing intense fracturing and pale green rim. Scanned polished thick-section. Blanca Dora pegmatite, sample GH253.

However, the contacts between gahnite and muscovite appear in places as irregular boundaries, and gahnite has fractures filled with muscovite (Fig. 2A, B, C, D). Some gahnite crystals have numerous fractures, occasionally exhibiting a yellow-brown staining (Fig. 2C, D). Muscovite is rich in small gahnite, quartz, and tiny opaque Fe oxide inclusions.

Tiny abundant inclusions are present along structurally controlled planes and concentrated in masses within gahnite (Fig. 2B). Gahnite from the La Ona and Sin Nombre pegmatites contains sparse, two-phase fluid inclusions of liquid and gas. Gahnite from the Blanca Dora, Magdalena, and Nancy pegmatites has abundant tiny inclusions of quartz, muscovite, and two-phase fluid inclusions of liquid and gas scattered throughout the crystals (Fig. 2B, C). These inclusions appear to be dispersed randomly with areas of high concentration forming dark zones and anastomosing lines.

Gahnite is commonly in contact with muscovite, quartz, and microcline. Quartz and microcline crystals do not contain inclusions of gahnite, but a few inclusions of quartz were observed in gahnite. Gahnite shows small inclusions and rims of muscovite near the edges of the crystals and within fractures (Fig. 3). Muscovite rims in gahnite and gahnite inclusions in muscovite may be the result of muscovitization of gahnite, in which case the gahnite most likely formed prior to muscovite (Fig. 2C). Quartz is known to form throughout the entire crystallization of the pegmatite melt. Therefore, the most likely order of formation of aluminous minerals is microcline – gahnite – muscovite.

### GAHNITE CHEMISTRY

Gahnite from the studied pegmatites is rich in zinc (34.6–39.7 wt.% ZnO), and has low Fe (4.8–9.0 wt.% FeO), and very low Mg (0.05–0.7 wt.% MgO) and Mn (0.26–0.92 wt.% MnO) contents (Tables 2, A1). The composition of the studied gahnite, expressed in mol.% of the spinel endmembers gahnite (Ghn), hercynite (Hc), spinel (Spl), galaxite (Glx), and magnetite (Mag) is defined by the ranges  $\text{Ghn}_{75.9-86.6}\text{Hc}_{7.1-20.0}\text{Spl}_{0.24-3.2}\text{Glx}_{0.66-2.3}\text{Mag}_{0-9.3}$  (Fig. 4A; Tables 2, A1). Gahnite from the La Ona pegmatite has the highest Zn contents and a compositional range expressed by  $\text{Ghn}_{79.7-86.6}\text{Hc}_{7.1-16.4}\text{Spl}_{0.26-0.8}\text{Glx}_{0.9-1.6}\text{Mag}_{0-7.1}$ , while gahnite from the Sin Nombre and Magdalena pegmatites has the lowest Zn and highest Fe contents and its compositional variations are defined by  $\text{Ghn}_{77.7-80.5}\text{Hc}_{14.3-18.8}\text{Spl}_{0.2-1.3}\text{Glx}_{0.75-1.4}\text{Mag}_{0-5.6}$  and  $\text{Ghn}_{76.80-84.5}\text{Hc}_{12.2-20.0}\text{Spl}_{0.4-1.6}\text{Glx}_{0.72-1.6}\text{Mag}_{0-5.4}$ , respectively. Gahnite compositions in the remaining pegmatites are defined by:  $\text{Ghn}_{76.4-82.1}\text{Hc}_{12.9-19.1}\text{Spl}_{0.3-1.1}\text{Glx}_{0.66-1.5}\text{Mag}_{0.69-7.1}$  for the Juan Román pegmatite,  $\text{Ghn}_{75.9-82.6}\text{Hc}_{7.6-15.5}\text{Spl}_{0.6-1.2}\text{Glx}_{1.0-1.8}\text{Mag}_{4.7-9.3}$  for the Blanca Dora pegmatite, and  $\text{Ghn}_{79.8-81.7}\text{Hc}_{8.4-12.1}\text{Spl}_{2.1-3.2}\text{Glx}_{1.7-2.3}\text{Mag}_{2.7-6.0}$  for the Nancy pegmatite.

Gahnite in the Nancy pegmatite, from the Conlara pegmatite district, has higher Mg and Mn contents than gahnite in pegmatites from the Comechingones pegmatite district, ranging from 2.08 to 3.19 mol.% spinel and from 1.69 to 2.26 mol.% galaxite endmembers (Fig. 4A, B; Tables 2, A1). Gahnite from the other pegmatites is characterized by low Mg and Mn contents, reaching values up to 1.59 mol.% spinel in the Magdalena pegmatite and up to 1.77 mol.% galaxite in the Blanca Dora pegmatite (Fig. 4A, B; Tables 2, A1). The anomalous Mg and Mn contents in gahnite from the Nancy pegmatite are distinct in the ternary diagrams of Figures 4A and 4B; on the other hand, the Mg and Mn contents of gahnite in the Comechingones district pegmatites show very limited variability, both within and among the pegmatites (Fig. 4A, B). The amount of  $\text{Fe}^{3+}$  in gahnite is relatively low, with the magnetite endmember component ranging from 0 to 9.3 mol.% and being highest in gahnite from the Blanca Dora pegmatite.

Weak and heterogeneous compositional zoning was identified in the gahnite by EMP transects across crystals ~20 mm in length. One type of pattern is defined by a variation towards the rim from 35.90 to 38.62 wt.% ZnO and 9.04 to 6.49 wt.% FeO (total iron). Variations of Mn follow that of Fe in some crystals but are small (<0.5 wt.% MnO), whereas changes in Mg are extremely small (<0.2 wt.% MgO) and do not follow a consistent pattern. In other crystals, fluctuations in Zn, Fe, Mn, and Mg can be observed within the crystals, whereas in the rim there is higher Zn and lower Fe than closer to the core. Backscattered electron images show the heterogeneous and slight compositional variations, mostly seen as changes in Zn closer to the rim (<300  $\mu\text{m}$  wide), as well as next to fractures filled with muscovite and next to rims with muscovite (Fig. 3).

A plot of molecular  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  versus  $(\text{Zn} + \text{Mn})/\text{Al}$  can be used to identify gahnite compositional variations (Batchelor & Kinnaird 1984; Fig. 5). In this diagram, gahnite from the Nancy pegmatite overlaps gahnite from the La Ona pegmatite. The lowest  $(\text{Zn} + \text{Mn})/\text{Al}$  ratios (0.391) and highest  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  ratios (0.107) correspond to gahnite from the Magdalena pegmatite, whereas the highest  $(\text{Zn} + \text{Mn})/\text{Al}$  ratios (0.460) and lowest  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  ratios (0.049) correspond to gahnite from the La Ona pegmatite. Gahnite from the La Ona pegmatite has the highest average  $(\text{Zn} + \text{Mn})/\text{Al}$  ratios ( $0.436 \pm 0.009$ ) and lowest average  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  ratios ( $0.072 \pm 0.006$ ).

### DISCUSSION

#### *Gahnite formation and occurrence*

Even though gahnite is an uncommon mineral, it has been known since the 1800s (*e.g.*, Dana 1904, Palache *et al.* 1944). One of the first published descriptions and

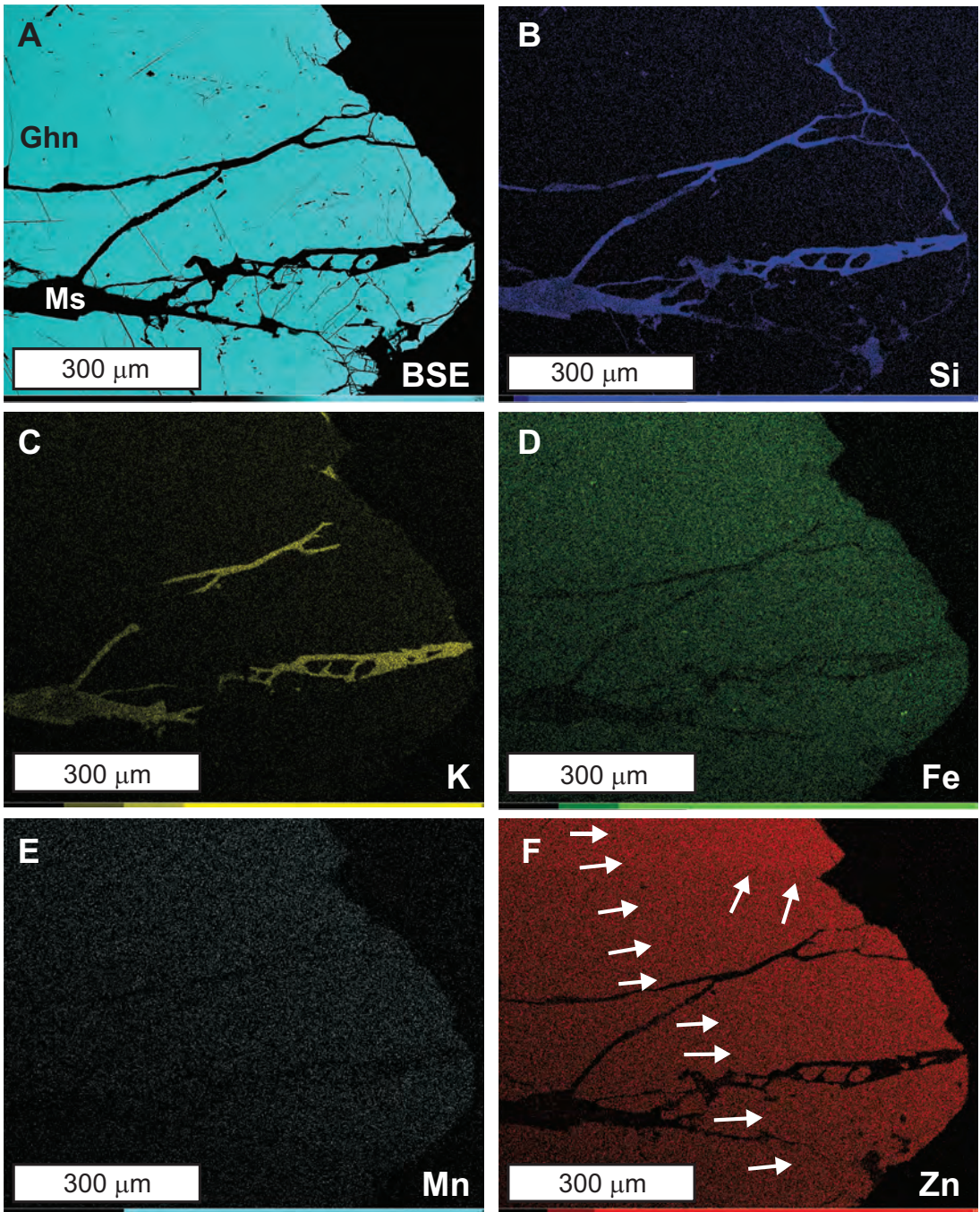


FIG. 3. Backscattered electron (BSE) images of gahnite (Ghn) from the Blanca Dora pegmatite (sample GH253) showing slightly higher Zn and lower Fe contents near the edge compared to inner portions of the crystal as well as muscovite-filled fractures. (A) Backscattered electron image. Note the darker and patchy color of gahnite surrounding “Ghn” and lighter color towards the right (edge). Muscovite (Ms) fills fractures and also appears as very thin rims at the edge of the crystal. (B) Si, and (C) K, showing the location of muscovite. (D) Fe. Note slightly darker very thin rim in upper right. (E) Mn. (F) Zn. Arrows point to the area where Zn contents become higher towards the right (edge of crystal) compared to the left. Two arrows in upper right point to the area with the highest Zn contents.



TABLE 2. REPRESENTATIVE COMPOSITIONS FOR GAHNITE FROM GRANITIC PEGMATITES OF THE PAMPEAN PEGMATITE PROVINCE, ARGENTINA\*

Sample #	Juan Román			La Ona			Blanca Dora			Magdalena			Sin Nombre			Nancy		
	1	2	3	4	5	6	7	8	9	10	11	12	13					
SiO <sub>2</sub> wt.%	0.00	0.02	0.00	0.02	0.00	0.00	0.10	0.06	0.04	0.09	0.00	0.03	0.03					
TiO <sub>2</sub>	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
Al <sub>2</sub> O <sub>3</sub>	54.29	54.86	54.73	54.64	54.42	53.89	55.64	55.24	56.16	55.04	55.12	55.92	55.20					
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.03	0.00	0.02	0.03	0.02	0.01					
FeO	8.74	6.69	7.50	4.81	9.04	6.49	8.32	5.66	8.14	7.23	6.15	5.71	6.13					
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00					
MgO	0.22	0.09	0.15	0.13	0.20	0.15	0.22	0.12	0.24	0.15	0.72	0.55	0.74					
MnO	0.55	0.35	0.58	0.36	0.65	0.41	0.54	0.30	0.46	0.30	0.90	0.74	0.74					
ZnO	35.56	37.33	37.20	39.69	35.90	38.62	34.64	38.13	35.62	36.50	37.36	37.60	37.29					
K <sub>2</sub> O	0.00	0.01	0.01	0.02	0.01	0.02	0.03	0.02	0.03	0.01	0.01	0.01	0.01					
Total	99.58	99.46	100.35	99.79	100.48	99.82	99.49	99.61	100.72	99.40	100.46	100.67	100.29					
<i>apfu based on 4 oxygen atoms</i>																		
Si	0.000	0.001	0.000	0.001	0.000	0.000	0.003	0.002	0.001	0.003	0.000	0.001	0.001					
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000					
Al	1.952	1.974	1.956	1.966	1.942	1.943	1.987	1.982	1.983	1.977	1.958	1.978	1.962					
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000					
Fe <sup>3+</sup>	0.047	0.025	0.045	0.033	0.058	0.057	0.008	0.014	0.015	0.018	0.042	0.020	0.036					
Fe <sup>2+</sup>	0.176	0.146	0.146	0.090	0.171	0.109	0.203	0.131	0.189	0.166	0.113	0.123	0.118					
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000					
Mg	0.010	0.004	0.007	0.006	0.009	0.007	0.010	0.006	0.011	0.007	0.032	0.025	0.033					
Mn	0.014	0.009	0.015	0.009	0.017	0.011	0.014	0.008	0.012	0.008	0.023	0.019	0.019					
Zn	0.801	0.841	0.833	0.895	0.802	0.872	0.775	0.857	0.788	0.821	0.831	0.833	0.830					
K	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000					
Total	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000					
Glx	1.366	0.875	1.424	0.912	1.577	1.016	1.369	0.750	1.144	0.749	2.206	1.855	1.814					
Spl	0.946	0.404	0.628	0.560	0.863	0.648	0.967	0.550	1.066	0.686	3.119	2.409	3.193					
Ghn	76.404	82.057	79.730	86.641	75.902	82.607	76.775	84.482	77.688	80.499	79.791	81.682	80.084					
Hc	14.507	13.049	11.796	7.080	13.414	7.588	19.666	12.195	17.851	15.398	8.842	11.116	9.652					
Mag	6.777	3.615	6.422	4.808	8.244	8.141	1.223	2.022	2.251	2.667	6.042	2.938	5.258					

\*Note: Fe<sup>3+</sup> calculated from stoichiometry assuming 4 O *apfu* and Al+Cr+Fe<sup>3+</sup>+Fe<sup>2+</sup>+Ca+Mg+Mn+Zn = 3. Sample numbers: 1, 2 – GH011; 3, 4 – GH243; 5, 6 – GH253; 7, 8 – GH273; 9 – GH274A; 10 – GH274B; 11-13 – NA001. Data obtained by EMPA.

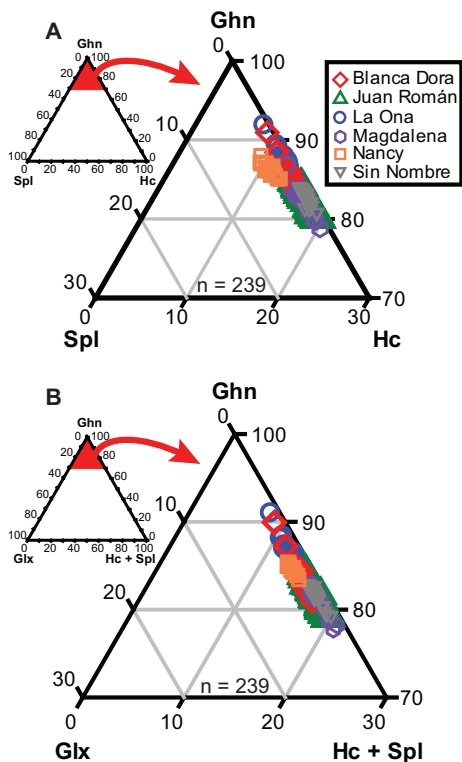


FIG. 4. Ternary diagrams of gahnite compositions in granitic pegmatites from the Pampean Pegmatite Province, Argentina, obtained in this study, in terms of: (A) Gahnite (Ghn, Zn), hercynite (Hc, Fe), and spinel (Spl, Mg) endmembers (in mol.%). After Němec (1973), Batchelor & Kinnaird (1984); and (B) Ghn, Hc + Spl, and Glx (galaxite, Mn) endmembers (in mol.%). Only the top 30% of the diagram is shown (Ghn endmember).

analyses of gahnite in the western world was from a pegmatite intruding gneisses near Träskböle in Perniö, Finland (Eskola 1914) (Table 3). A few studies of the occurrence of gahnite in granitic pegmatites were done in Europe and North America during the mid-1900s (e.g., Pehrman 1948, von Knorring & Dearnley 1960). In the 1970s to 90s more detailed chemical studies of gahnite in granitic pegmatites emerged (e.g., Němec 1973, Jackson 1982, Batchelor & Kinnaird 1984, Spry & Scott 1986b, Alfonso *et al.* 1995, Morris *et al.* 1997, Neiva & Champness 1997, Tindle & Breaks 1998, Li *et al.* 1999a).

In granitic pegmatites, gahnite, and sphalerite are the main Zn-bearing minerals (Černý & Hawthorne 1982). Their crystallization is controlled by the activity of S in the melts and the availability of Zn and Al; sphalerite is likely to form in sulfide-rich pegmatite melts while gahnite forms in sulfide-poor pegmatite melts (Černý & Hawthorne 1982). The studied

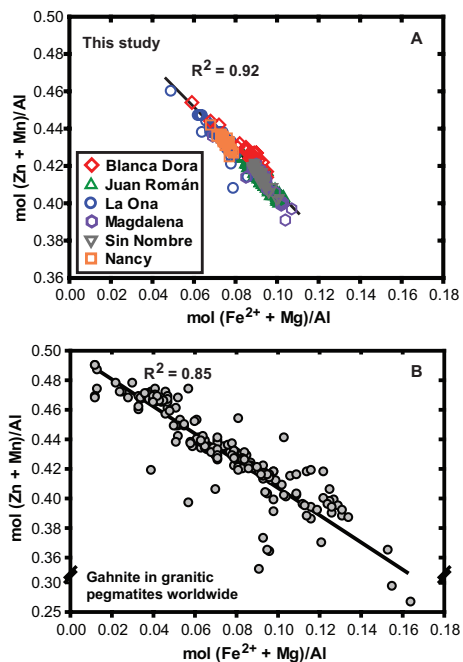


FIG. 5. Binary diagram showing the composition of gahnite from granitic pegmatites of the Comechingones and Conlara pegmatite districts (A) and gahnite from worldwide granitic pegmatites (B) in terms of molecular  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  versus  $(\text{Zn} + \text{Mn})/\text{Al}$ . After Batchelor & Kinnaird (1984). Data in (B) from references reported in Table 3.

pegmatites from the Comechingones pegmatite district do not contain sulfide minerals and the chemistry of the melts resulted in the crystallization of gahnite rather than sphalerite. The Nancy pegmatite from the Conlara pegmatite district hosts minor sulfides in phosphate nodules, including sphalerite, and it may represent a melt of higher S content compared with the Comechingones pegmatite melts. This higher content of S could be explained by compositional differences between pegmatite melts as well as different host rocks compared to those for the pegmatites of the Comechingones pegmatite district. Pegmatites in this district are hosted by augen-gneiss and cordierite migmatite of the Guacha Corral Shear Zone while the Nancy pegmatite from the Conlara pegmatite district is hosted by medium-grade gneiss of the Conlara Metamorphic Complex. The presence of sulfide minerals and the host rock difference are also reflected in the higher Mg and Mn content in gahnite from the Nancy pegmatite compared with gahnite from pegmatites of the Comechingones district (see below for elaboration).

Gahnite in granitic pegmatites is known to occur with and contain inclusions of quartz, albite,

TABLE 3. SUMMARY INFORMATION FOR GRANITIC PEGMATITES WITH GAHNITE COMPOSITIONS REPORTED IN THE LITERATURE

Name, Location	Host Rock	Classification	Mineralogy	Rare-metals	Age (Ma)	References
Altai, Keketuohai, Xinjian, China	Amphibolite	REL-Li (LCT)	Ab, Brl, Ghn, Mag, Mc, Ms, Plc, Qz, Rt, Spd, Tur	Be, Li, Nb, Ta, REEs	218.4 ± 5.8	18, 19, 35, 37
Alto Mirador, BPP, Brazil	Quartzite	REL-Li – lepidolite subtype (LCT)	Ab, Ap, Brl, Bt, Cbl, Cld, Eul, Ghn, Grt, Lpd, Mlc, Ms, Qz, Ttl, Tur, Zrn	Be, Li, Ta	480 – 520	27, 28
Auburn, Maine, USA	Metasedimentary rocks	REL-Li – beryl-columbite-phosphate subtype (LCT)	Ab, Ap, Brl, Bt, Cst, Ghn, Grt, Isk, Lpd, Mc, Mlt, Ms, Pl, Qz, Spd, Trp, Tur, Zrn	Be, Li, Sn	325 ± 3	29, 36
Burteson Mica Mine, Spruce Pine, NC, USA	Amphibolite	MSREL	Brl, Bt, Col, Ghn, Grt, Ms, Pl, Qz, Tur	Be, Nb	377 – 404	29, 30
Cabanas, Portugal	Mica schist	REL-Li (LCT)	Ab, Ap, Apy, Brl, Ccp, Col-Ttl, Cst, Ghn, Grt, Ilm, Mc, Mtb, Mnz, Ms, Or, Po, Py, Qz, Rt, Sil, Sp, Tpz, Tur, Znw, Zrn	Be, Nb, REEs, Sn, Ta		24
Cáceres, Spain	Metasedimentary rocks	–	Ap, Brl, Cbl, Kfs, Ms, Pl, Qz	Be	312 – 328	20
Capoeira 2, BPP, Brazil	Metacglomerate	REL-Li (LCT)	Ab, Ap, Cld, Col, Drv, Elb, Ghn, Grt, Mc, Ms, Qz, Spd, Srl, Ixo, Umit	Li, Nb, Sn, Ta, Ti, U	480 – 520	27, 28
Cap de Creus, Spain	Andalusite-cordierite schist	REL-Li – beryl-columbite subtype (LCT)	And, Apy, Brl, Cbl, Col, Ghn, Ixo, Kfs, Ms, Qz, Sil, Srl, Urm, Wfm	Be, Ta, U, W	280 – 310	1, 2, 3; 7
Chiapaval, South Harris, Scotland	–	–	Ab, Aln, Brl, Bt, Col, Ghn, Grt, Mag, Mc, Mrz, Ms, Py, Qz, Thr, Tur, Urm, Zrn	Nb, REEs, Th, U	1,700	10, 34
Jemaa, Nigeria	Hornblende-biotite gneiss	(LCT)	Ab, Cst, Ghn, Ms, Qz, Srl, Ttl	Sn, Ta	450 – 500	4, 15
Lord Hill, Stoneham, Maine, USA	Diorite	REL-Li – beryl-columbite-phosphate subtype (LCT)	Ap, Brl, Bt, Cld, Col, Crl, Fl, Ghn, Ms, Pl, Py, Qz, Tpz, Tph, Trp, Zrn	Be, Nb	325 ± 3	17, 29, 36
Mufushan, Pingjiang, China	Monzogranite	REL-Li (LCT)	Ab, Brl, Bt, Col, Ghn, Mag, Mc, Mnz, Ms, Qz, Ttl	Be, Nb, Ta, REEs	96 – 136	18, 19
Namivo, Alto Ligonha, Mozambique	Migmatitic paragneiss	REL-Li – lepidolite subtype (LCT)	Ab, Brl, Bt, Col, Cst, Ghn, Grt, Kfs, Lpd, Ms, Qz, Rt, Ttl, Tur, Znw	Be, Li, Nb, Sn, Ta, Ti		23, 25
Quintos, BPP, Brazil	Quartzite	REL-Li (LCT)	Ab, Brl, Bt, Nbs, Elb, Ghn, Grt, Lpd, Ms, Qz, Spd, Ixo, Tur, Umit	Be, Cs, Li, Ti, U	480 – 520	27, 28

TABLE 3. (CONTINUED)

Name, Location	Host Rock	Classification	Mineralogy	Rare-metals	Age (Ma)	References
Rosendal, Kimito, Finland	Hornblende gabbro	–	Ghn, Grt, Kfs, Ms, Pl, Qz, Sp			<b>26</b>
Separation Rapids, Ontario, Canada	Mafic meta-volcanic rock	REL-Li – petalite subtype (LCT)	Ab, Ald, Aln, Amp, Apy, Bri, Bt, Ccp, Col, Crd, Cst, Ep, Fsp, Fl, Fap, Ghn, Grt, Ilm, Kfs, Lo, Lpd, Mlt, Mnz, Ms, Ngd, Plc, Plt, Prp, Py, Qz, Sch, Sp, Spd, Sbt, Srv, Tpz, Ttl, Tur, Urm, Wdg, Xtm, Ypd, Znw, Zrn	As, Be, Li, Nb, REEs, Sn, Ta	2,643 ± 2	<b>8, 21, 32</b>
Serra de Arga, Portugal	Mica schist	–	Ab, Ap, Bri, Bt, Cbl, Chl, Col, Cst, Ghn, Ms, Ngd, Or, Qz, Rt, Spd, Tpz, Ttl, Znw, Zrn	Be, Li, Nb, Sn, Ta	300 – 310	<b>5, 12, 22</b>
Siedlimowice, Poland	Two-mica granite	REL-Li – beryl-columbite subtype (LCT)	Ap, Bri, Bt, Chl, Col, Ghn, Grt, Kfs, Ms, Pl, Qz, Zrn	Be, Nb		<b>6, 16, 31, 33</b>
Topsham, Maine, USA	Gneiss	REL-REE subclass (NYF)	Ab, Kfs, Qz, Bt, Ms, Ghn, Bri, Col, Tpz, Mag, Mnz, Tur	Nb, REEs, Ta, Ti	367 ± 4	<b>13, 29, 36</b>
Träskböle, Finland	Gneiss	–	Ab, Bt, Ccp, Chl, Qz, Ghn, Mc, Ms, Pl, Po, Py, Sp		1,800	<b>9, 14</b>
Vírocco, Argentina	Gabbro, norite	Abyssal + rare-element class (LCT)	Qz, Ab, Pl, Tur, Dum, Ms, Ky, Bri, Cbl, Grt, Fap, Col-Ttl, Plc, Ghn, Zrn, Urm, Thr	Cs, Ta, Be	–	<b>11</b>

Mineral abbreviations (\* Denotes those from Whitney & Evans 2010): Albite – Ab\*, Allanite – Aln\*, Alluaudite – Ald, Amphibole – Amp\*, Andalusite – And\*, Apatite – Ap\*, Arsenopyrite – Apy, Bertrandite – Btr, Beryl – Brl\*, Biotite – Bt\*, Brannerite – Brr, Cassiterite – Cst\*, Chalcopyrite – Ccp\*, Chlorite – Chl\*, Chrysoberyl – Cbl, Cleavelandite – Cld, Columbite – Col, Cordierite – Crd\*, Cryolite – Crf\*, Dravite – Drv\*, Dumortierite – Dum\*, Elbaite – Elb\*, Epidote – Ep\*, Euclase – Eul, Ferrotapolite – Ftp, Fluorapatite – Fap, Fluorite – Fl\*, Garnet – Grt\*, Gahnite – Ghn\*, Garnet – Grt\*, Ilmenite – Ilm\*, Ixiolite – Ixo, K-feldspar – Kfs\*, Kyanite – Ky\*, Lepidolite – Lpd\*, Löllingite – Lo\*, Magnetite – Mag\*, Malachite – Mlc\*, Metatorbernite – Mtb, Microcline – Mc\*, Microilite – Mlt, Monazite – Mnz\*, Muscovite – Ms\*, Natrobastanite – Nbs, Nigelite – Ngd, Orthoclase – Or\*, Petalite – Ptl\*, Plagioclase – Pl\*, Pollucite – Plc, Purpurite – Prp, Pyrite – Py\*, Pyrrhotite – Po\*, Quartz – Qz\*, Rutile – Rt\*, Samarskite – Smk, Scheelite – Sch\*, Schorl – Scl\*, Sillimanite – Sil\*, Sphalerite – Sp\*, Spodumene – Spd\*, Stibiobetafite – Sbt, Struvite – Srv, Tantalite – Ttl, Thorite – Thr\*, Topaz – Tpz\*, Triplite – Trp, Triphylite – Tph, Tourmaline – Tur\*, Uraninite – Urm\*, Uranomicroilite – Umit, Wodginit – Wdg, Wolframite – Wfm, Xenotime – Xtm\*, Yttrpyrochlore – Ypd, Zinnwaldite – Znw\*, Zircon – Zrn\*.

Abbreviations for pegmatite nomenclature, based on the classification of Černý & Erat (2005) and Černý *et al.* (2012): REL – rare-element class; MSREL – muscovite rare-element class; Li – Li subclass; REE – rare-earth element subclass; LCT – lithium, cesium, tantalum pegmatite family; NYF – niobium, yttrium, fluorine pegmatite family. Location abbreviations: BPP – Borborema Pegmatite Province.

References (bold numbers in Table indicate those with garnite compositions): 1 Alfonso & Melgarejo (2008); 2 Alfonso *et al.* (1995); 3 Alfonso *et al.* (2003); 4 Batchelor & Kinnaird (1984), 5 Dias (2011), 6 Domanska-Sluda (2007), 7 Druguet & Hutton (1998), 8 Dunlop (2000), 9 Eskola (1914), 10 Fettes & Mendum (1987), 11 Galliski *et al.* (2012), 12 Gomes *et al.* (1995), 13 Hanson *et al.* (1998), 14 Huhma (1986), 15 Jackson (1982), 16 Janeczek (2007), 17 Johnson (1998), 18 Li *et al.* (1999a), 19 Li *et al.* (1999b), 20 Merino *et al.* (2013), 21 Morris *et al.* (1997), 22 Neiva *et al.* (1997), 23 Neiva (2013), 24 Neiva & Champress (1997), 25 Neiva & Neiva (2005), 26 Pehrman (1948), 27 Soares *et al.* (2007), 28 Soares *et al.* (2008), 29 Spry & Scott (1986b), 30 Swanson & Veal (2010), 31 Szuszkiewicz & Lobos (2004), 32 Tindle & Breaks (1998), 33 Turniak *et al.* (2007), 34 von Knorring & Deamley (1960), 35 Windley *et al.* (2002), 36 Wise & Francis (1992), 37 Zhu *et al.* (2006).

muscovite, tourmaline, garnet, beryl, zircon, columbite, and nigerite, and occasionally sphalerite (*e.g.*, Eskola 1914, Černý & Hawthorne 1982, Jackson 1982, Neiva & Champness 1997, Li *et al.* 1999a, Szuskiewicz & Łobos 2004, Soares *et al.* 2007). Because gahnite is a peraluminous mineral it will form in granitic pegmatites when there is excess Al and available Zn (Clarke 1981, Černý & Hawthorne 1982, Morris *et al.* 1997). Feldspars are typically the first aluminosilicate minerals to crystallize in granitic pegmatites, and if  $\text{Al}_2\text{O}_3$  is available after their crystallization, other aluminous minerals such as garnet, muscovite, and gahnite may form (von Knorring & Dearnley 1960, Clarke 1981, Černý & Hawthorne 1982, Hess 1989).

Based on the extensive compilation of gahnite occurrences and compositions done for this study, the occurrence of gahnite has been reported almost exclusively from LCT pegmatites, whereas its presence was described only in only one granitic pegmatite from the Spruce Pine district, NC, USA, which belongs to the muscovite-rare element class and may be of the NYF (niobium, yttrium, fluorine) family (Table 3; Spry & Scott 1986b). Gahnite also occurs coexisting with quartz, plagioclase, and muscovite in a pegmatite of the Topsham district, Maine (Spry & Scott 1986b), that likely corresponds to a poorly to moderately fractionated rare-element class, rare earth element subclass pegmatite (Wise & Francis 1992; Table 3) of the NYF family that also contains beryl, topaz, biotite, almandine, and magnetite as accessory minerals. However, the exact location of this sample was not known at the time of publication and it is uncertain whether it is derived from an NYF or LCT pegmatite. Gahnite occurrences, therefore, are more common in peraluminous pegmatites of the LCT family that have excess  $\text{Al}_2\text{O}_3$  available to form gahnite and they are very rare in NYF family pegmatites that tend to be metaluminous.

#### *The relationship between gahnite chemistry, pegmatite mineralogy, and pegmatite fractionation*

Gahnite from the Nancy pegmatite and the pegmatites of the Comechingones district is slightly different compositionally (Figs. 4A, 6). In most cases, the concentrations of Mg and Mn are typically low or absent in gahnite from granitic pegmatites, since other minerals (*e.g.*, tourmaline, garnet) incorporate Mg and Mn before or during the crystallization of gahnite (*e.g.*, Tulloch 1981). It would be expected that the elevated contents of Mg and Mn in gahnite from the Nancy pegmatite would also be reflected in the accessory mineralogy of the host pegmatite. The presence of Mn-rich fluorapatite, ( $\text{Fe}^{2+}$ ,Mg)-bearing bobfergusonite  $[\text{Na}_2\text{Mn}_3\text{Fe}^{3+}\text{Al}(\text{PO}_4)_6]$ , and Mn-rich wyllieite  $[(\text{Na,Ca,Mn}^{2+},\square)_2\text{Mn}^{2+}_2\text{Al}(\text{PO}_4)_3]$  in the Nancy pegmatite (Tait *et al.* 2004) suggests that its pegmatite melt had elevated Mn and Mg contents

during the formation of gahnite. These minerals are absent in the pegmatites of the Comechingones district, suggesting that the melts likely had lower Mn contents than that of the Nancy pegmatite, and this is also reflected in the composition of the gahnite.

The elevated Mg content in gahnite (and bobfergusonite) from the Nancy pegmatite can be explained by several alternative or combined factors: (1) differences in host rocks compared with the Comechingones pegmatites and assimilation of Mg-rich host rock (which is, however, unknown at the Nancy pegmatite locality) could have provided additional Mg to the system; (2) a different melt source slightly higher in Mg; (3) lower abundance of other Mg-bearing minerals such as garnet (with low Mg in the Nancy pegmatite), and minor tourmaline, a mineral whose early crystallization commonly depletes the pegmatitic melts in Mg; and (4) the unique presence of sphalerite, which could decrease the amount of Zn in the system in the case of early (or simultaneous with gahnite) crystallization. The combination of the presence of sphalerite and minor occurrence of tourmaline in the Nancy pegmatite seems the most likely explanation for the compositional differences in gahnite from this pegmatite *versus* the Comechingones pegmatites. However, due to the limited chemical information available for other minerals, the elevated Mg content in gahnite from the Nancy pegmatite cannot be explained satisfactorily until more mineral-chemical studies are conducted.

Based on the mineralogy and major mineral chemistry (*i.e.*, feldspars), the degree of evolution of the pegmatites generally increases towards the south of the district (Demartis *et al.* 2012, Galliski & Sfragulla 2014). The La Ona and Juan Román pegmatites are located in the southern portion of the district and are part of the same group (Co. Las Ovejas; Table 1; Fig. 1), but their gahnite does not reflect the same degree of evolution. The La Ona pegmatite is considered the most evolved pegmatite of the district and it contains Be (beryl), Nb (columbite-group minerals), phosphates, and uranium minerals, the latter not found in the Juan Román pegmatite (Hub 1994, Galliski 1999a, Galliski & Sfragulla 2014; Table 1). The mineralogy and the highest Zn content of gahnite in the La Ona pegmatite indicate that it is the most evolved pegmatite. Gahnite from the Juan Román pegmatite has slightly lower Zn contents than that from the La Ona pegmatite and it lacks uranium minerals, which indicates a lower degree of evolution for the former.

The Sin Nombre, Magdalena, and Blanca Dora pegmatites are located further to the north (than the La Ona and Juan Román pegmatites), belong to different groups of pegmatites, and based on their mineralogy are generally less evolved than the pegmatites to the south, which is reflected in the composition of the gahnite (Table 1; Hub 1994, Galliski 1999a, Demartis *et al.* 2012, Galliski & Sfragulla 2014). The Sin Nombre pegmatite contains garnet, beryl,

tourmaline (schorl), apatite, and autunite, and is considered the least evolved pegmatite. It is classified as a muscovite-rare element class, Li subclass pegmatite, whereas the rest of the studied pegmatites belong to the rare-element class, Li subclass (Table 1). The Magdalena, Juan Román, and Blanca Dora pegmatites contain fluorapatite and columbite-group minerals, reflecting their higher degree of evolution compared with the Sin Nombre pegmatite, which lacks the latter mineral. The Magdalena and Juan Román pegmatites have the same mineralogy and are expected to have similar gahnite compositions, and their compositions in fact overlap (Figs. 4, 5A). Gahnite from the Magdalena pegmatite has the lowest Zn contents (34.6 wt.% ZnO; 78.5 mol.% gahnite endmember), but overall is similar to gahnite from the Juan Román and Sin Nombre pegmatites. Because gahnite from the Juan Román and Magdalena pegmatites reaches higher Zn contents than that from the Sin Nombre pegmatite, the former pegmatites have a higher degree of evolution compared with the latter, consistent with mineralogical evidence. The lowest Zn contents in gahnite from the Blanca Dora pegmatite are higher than those in gahnite from the Sin Nombre, Magdalena, and Juan Román pegmatites, and attain the middle of the compositional field of gahnite from Argentina, reflecting an intermediate degree of evolution. Therefore, based on the mineralogy and Zn content of gahnite, the order of increasing melt evolution for these pegmatites is: Sin Nombre → Magdalena → Juan Román → Blanca Dora → La Ona. We note here that the pegmatites do not belong to the same group and not all are comagmatic. Therefore, the interpretation of the relative degree of evolution inferred from the composition of gahnite is not meant to speak of a single melt that evolved to form the various pegmatites.

#### *Gahnite compositional variations among pegmatites and pegmatite fractionation*

The plot of molecular  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  versus  $(\text{Zn} + \text{Mn})/\text{Al}$  in gahnite has been used to understand the substitutions or solid-solutions involving Zn,  $\text{Fe}^{2+}$ , Mn, and Mg, as well as the degree of evolution of the host pegmatites (Fig. 5; Batchelor & Kinnaird 1984, Tindle & Breaks 1998, Soares *et al.* 2007). The compositions of gahnite from Argentina pegmatites studied here and those from the literature of granitic pegmatites worldwide are shown in this diagram (Fig. 5A, B, Table 3). Gahnite compositions from Argentina fall within the field defined by Batchelor & Kinnaird (1984) for igneous gahnite and plot in the middle of the overall gahnite compositional field, with similarity to gahnite from the pegmatites at Separation Rapids, Canada (Tindle & Breaks 1998), and the Lord Hill and Topsham pegmatites, Maine (Spry & Scott 1986b) (Fig. 5; Table 3).

In this diagram, the data are expected to plot in a linear fashion with a slope of  $-1$  for perfect substitution conditions between  $\text{Fe} + \text{Mg}$  and  $\text{Zn} + \text{Mn}$  (Batchelor & Kinnaird 1984) (*i.e.*,  $\text{R}^{2+}$  site = 1) when the magnetite component ( $\text{Fe}^{3+}$ ) is absent (*i.e.*,  $\text{R}^{3+}$  site is full with Al = 2 atoms per formula unit for 4 anions), and/or if other components are absent. The best fit of a line through the data for gahnite from the Argentina pegmatites yields an  $\text{R}^2$  of 0.92 and a slope of  $-1.12$  (Fig. 5A). All previously published compositions of gahnite in granitic pegmatites define a line with  $\text{R}^2 = 0.85$  and slope =  $-1.04$  (Fig. 5B). This relatively low  $\text{R}^2$  for the Argentina data, and the even lower value for all the gahnite data, is attributed to substitutions taking place in the gahnite structure other than the ones considered in this diagram or the presence of  $\text{Fe}^{3+}$  in some crystals, and this is investigated below with alternative parameters for the Argentina gahnite.

First, we investigated correlations of Mg with  $\text{Fe}^{2+}$  and Zn (Fig. 6 A, B) and of Mn with  $\text{Fe}^{2+}$  and Zn (Fig. 6C, D), which are not significant. The binary plots are useful to distinguish gahnite from the various pegmatites, and in particular that from the Nancy pegmatite. Manganese and Mg are very low and do not vary much among gahnite samples from the Comechingones district, but they differ in the relative amount of Zn and  $\text{Fe}^{2+}$  (Fig. 6). Since Mn and Mg are low and Zn/ $\text{Fe}^{2+}$  ratios in gahnite have been used to infer the relative degree of evolution of pegmatites, in which Zn increases with fractionation (Batchelor & Kinnaird 1984, Soares *et al.* 2007), a plot of molecular  $\text{Fe}^{2+}$  versus Zn was next used to evaluate this substitution and the relative degree of evolution of the pegmatite melts (Fig. 7A; Table 2). Gahnite from Comechingones plots along a line with  $\text{R}^2 = 0.96$  and slope =  $-0.99$ . Gahnite from the Nancy pegmatite does not follow the same linear trend and defines a different array with  $\text{R}^2 = 0.60$  and slope =  $-0.52$  that falls below (lower Fe for a given Zn content) the data for gahnite from the Comechingones pegmatites. This low correlation in gahnite from the Nancy pegmatite is the result of both its higher Mn and Mg contents compared with the other gahnite analyzed and the likelihood that Zn is substituted by these elements.

Ranges and average Zn/ $\text{Fe}^{2+}$  ratios in gahnite from the Comechingones pegmatites decrease from a maximum for La Ona (4.94–9.98; avg. = 6.252) to Blanca Dora (4.41–8.02; avg. = 5.225), and are similar and lower in the Sin Nombre (4.18–4.94; avg. = 4.611), Magdalena (3.83–6.57; avg. = 4.594), and Juan Román (3.99–5.76; avg. = 4.587) samples. Based on the highest Zn/ $\text{Fe}^{2+}$  ratios among gahnite with very low to nil Mn and Mg values from these pegmatites, gahnite from the La Ona pegmatite reflects the most evolved melts, which is consistent with its highest Zn and low Fe contents ( $\text{Ghn}_{85-88}\text{Hc}_{9,1-12,7}\text{Spl}_{2,2-3,4}$ ) and the mineralogical evidence presented above. The Sin Nombre,

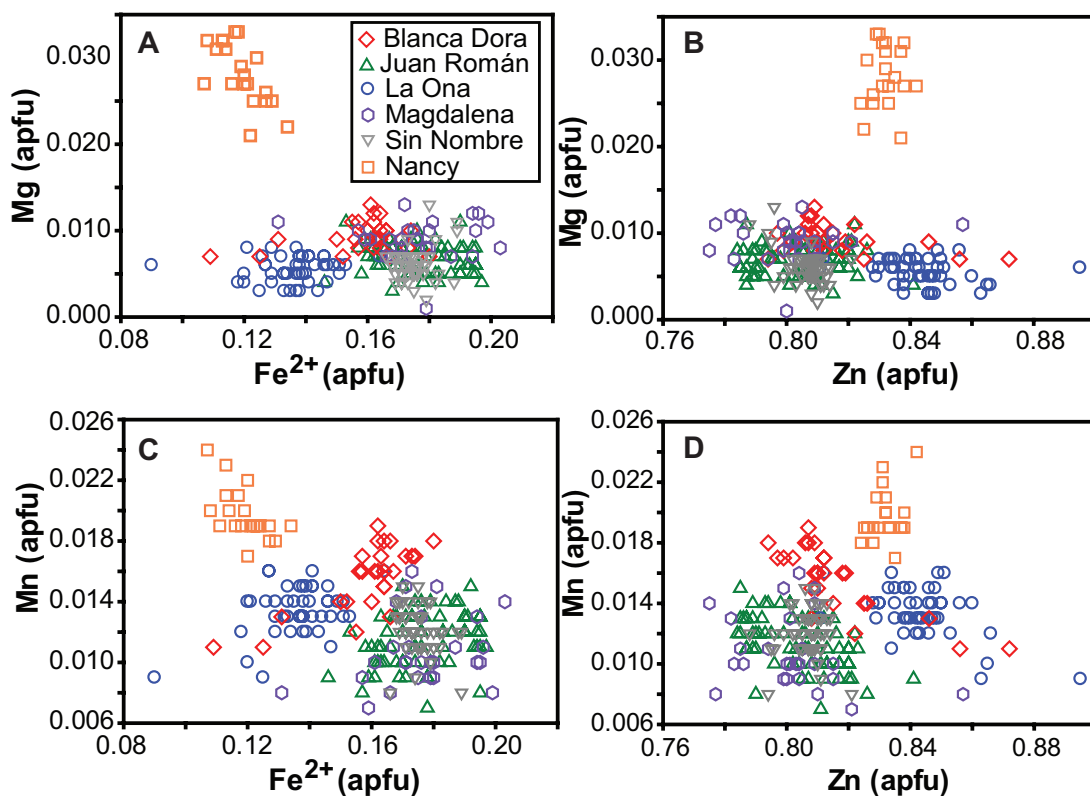


FIG. 6. Binary diagrams showing the composition of gahnite in pegmatites from the Pampean Pegmatite Province (in *apfu*) in terms of: (A)  $\text{Fe}^{2+}$  versus Mg. (B) Zn versus Mg. (C)  $\text{Fe}^{2+}$  versus Mn. (D) Zn versus Mn. *apfu* – atoms per formula unit based on 4 oxygen atoms.

Magdalena, and Juan Román pegmatites are interpreted to be the least evolved pegmatites of the district based on the location of gahnite in the Zn versus  $\text{Fe}^{2+}$  diagram, which is also consistent with Zn contents in the gahnite and the mineralogical evidence. However, gahnite from the Juan Román pegmatite has mostly intermediate Zn and  $\text{Fe}^{2+}$  contents and Zn/ $\text{Fe}^{2+}$  ratios, and based on its mineralogy the pegmatite is more evolved than the Magdalena and Sin Nombre pegmatites. Because the compositional variation in gahnite from the Juan Román pegmatite attains higher Zn and lower  $\text{Fe}^{2+}$  contents than gahnite in the Sin Nombre pegmatite, the former pegmatite is interpreted to be more evolved. Furthermore, even though gahnite from the Nancy pegmatite has very high Zn/ $\text{Fe}^{2+}$  ratios (6.15–7.89; avg. = 7.003), they reflect its somewhat lower  $\text{Fe}^{2+}$  and Zn contents, but most importantly its higher Mg and Mn contents compared to gahnite from the La Ona pegmatite, which has the highest Zn/ $\text{Fe}^{2+}$  ratios, higher (Zn + Mn)/Al ratios, and lower ( $\text{Fe}^{2+}$  + Mg)/Al ratios (Figs. 5, 6, 7A). The substitutions of Mg and Mn in gahnite from the Nancy pegmatite are significant, and this gahnite reflects a lower degree of evolution compared with that

from the La Ona pegmatite. Therefore, this shows that Zn/ $\text{Fe}^{2+}$  ratios in gahnite alone may not be the best indication of pegmatite evolution if other elements are present in the gahnite structure, and in this case it needs to be placed in the context of all other chemical information. Thus, along with  $\text{Fe}^{2+}$ , the Mn and Mg contents in gahnite were considered next as substitutions for Zn to better determine pegmatite melt evolution.

A new plot of molecular Zn versus ( $\text{Fe}^{2+}$  + Mg + Mn) shows a very good linear correlation ( $R^2 = 0.9932$ ; slope =  $-0.995$ ) with all the data from the Argentina pegmatites plotting along the same line, indicating that these parameters represent well the substitutions [Zn for ( $\text{Fe}^{2+}$  + Mg + Mn)] in gahnite (Fig. 7B). Now gahnite from the Nancy pegmatite plots in a similar way to that from the La Ona pegmatite with lower Zn and higher ( $\text{Fe}^{2+}$  + Mg + Mn) contents, consistent with the interpretation above regarding relative melt fractionation. Gahnite compositions from worldwide pegmatites plotted in this diagram (not shown) yield a good correlation ( $R^2 = 0.929$ ; slope =  $-1.038$ ) that is also better than that obtained using the Batchelor & Kinnaird (1984)

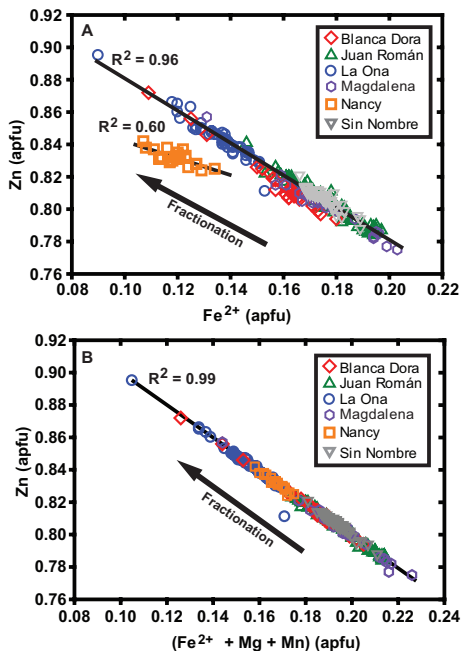


FIG. 7. Binary diagram showing the composition of gahnite in granitic pegmatites obtained in this study (in *apfu*) in terms of: (A)  $\text{Fe}^{2+}$  versus Zn. (B)  $(\text{Fe}^{2+} + \text{Mg} + \text{Mn})$  versus Zn. The best linear correlation is observed in B. Arrows indicate the direction of increasing fractionation given by rising Zn contents.

diagram, reinforcing the idea that this diagram is more useful for determining melt evolution and substitutions in gahnite.

Finally, a new plot of molecular  $(\text{Fe}^{2+} + \text{Mg})$  versus  $(\text{Zn} + \text{Mn})$  was constructed to further investigate the substitutions and compositional variations of gahnite using only the elements common at the A site (Zn,  $\text{Fe}^{2+}$ , Mn, and Mg) (Fig. 8). The Argentina data now define an even better correlation ( $R^2 = 0.9937$ , slope =  $-0.996$ ) and the composition of gahnite from the Nancy pegmatite shifts to the right to join that of the gahnite from the La Ona pegmatite. Data for gahnite from pegmatites worldwide published in the literature (not shown) yield a better correlation than the previous diagram as well ( $R^2 = 0.936$ , slope =  $-1.04$ ). Therefore, for all the gahnite compositions available from granitic pegmatites Zn + Mn are inversely correlated with  $\text{Fe}^{2+} + \text{Mg}$ , and this plot best displays the substitutions within the gahnite crystal structure in these crystals (Zn + Mn for  $\text{Fe}^{2+} + \text{Mg}$ ) and the continuous solid-solution of gahnite and hercynite and minor spinel and galaxite. Since the former two elements tend to become concentrated as fractional crystallization progresses, whereas the last two do the opposite, the diagram is also an indication of relative degree of evolution of the pegmatite melts.

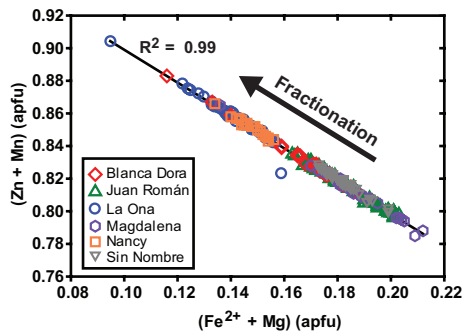


FIG. 8. Binary diagram showing the compositional variation and possible substitutions of gahnite in granitic pegmatites obtained in this study in terms of molecular  $(\text{Fe}^{2+} + \text{Mg})$  versus  $(\text{Zn} + \text{Mn})$  (*apfu*) based on 4 oxygen atoms). These variables define the best (negative) linear correlation for the studied samples, indicating that  $\text{Fe}^{2+} + \text{Mg}$  are likely substituted by Zn + Mn with increasing melt evolution.

This new diagram illustrates that gahnite in the Nancy pegmatite reflects a slightly lower degree of evolution than that from the La Ona pegmatite, which is consistent with the information presented previously (Fig. 8). This diagram also displays a wider range of compositions in gahnite from the Magdalena pegmatite that reaches higher Zn + Mn values than gahnite from the Sin Nombre pegmatite, consistent with the Magdalena pegmatite being slightly more fractionated than the Sin Nombre pegmatite. In summary, this diagram shows the following overall order of evolution among the pegmatites, from low to high: Sin Nombre  $\rightarrow$  Magdalena  $\rightarrow$  Juan Román  $\rightarrow$  Blanca Dora  $\rightarrow$  Nancy  $\rightarrow$  La Ona. This order differs somewhat from the order obtained using average Zn/ $\text{Fe}^{2+}$  ratios in gahnite but is consistent with that obtained from Zn contents in gahnite and pegmatite mineralogy. We consider that the parameters of Figure 8 better reflect the degree of evolution of gahnite and its host pegmatites because it incorporates only the major elements that are known to increase or decrease with fractional crystallization.

#### Compositional variations within gahnite crystals

Gahnite in granitic pegmatites is generally compositionally homogenous with respect to major elements (Batchelor & Kinnaird 1984, Szuszkiewicz & Łobos 2004, Soares *et al.* 2007), in contrast to that in rocks spatially associated with or in metamorphosed massive sulfide deposits in which it is commonly zoned (Spry 1987). In rare cases gahnite from pegmatites was found to display complex and irregular zoning (Leal Gomes *et al.* 1995, Merino *et al.* 2013, Neiva 2013). Zoning in gahnite in pegmatites is more likely



to occur in small crystals (<400  $\mu\text{m}$ ) than in larger crystals. When zoning is present in gahnite from these rocks, it exhibits enrichment in Zn and depletion in Fe and Mg in the rim compared to the core (Dunlop 2000, Neiva 2013), which is consistent with the enrichment of Zn in residual melts during magmatic differentiation (e.g., Tulloch 1981, Batchelor & Kinnaird 1984, Soares *et al.* 2007, Merino *et al.* 2010, 2013). However, two studies of pegmatites from Spain and Portugal found reversely zoned gahnite crystals, with enrichment of Zn and Mn and depletion of Fe and Mg in the core compared to the rim (Leal Gomes *et al.* 1995, Merino *et al.* 2013). These authors attributed the reversed zoning to an unidentified process (Leal Gomes *et al.* 1995, Merino *et al.* 2013), but it is consistent with the reversed chemical zoning seen at the pluton scale in the Spanish locality.

Gahnite from the studied Argentina pegmatites attains several centimeters in size. It is not expected that these large gahnite crystals would record marked compositional zoning, and indeed the majority of the samples investigated here do not display clear compositional changes between core and rim. In fact, most of the large crystals of gahnite that were analyzed with transects exhibit small random variations of Zn, Fe, Mn, and Mg from core to rim. This could be the result of the orientation of the analyzed crystals, the measurements not covering the entire crystal, and/or because some samples are mineral separates and perhaps incomplete crystals. However, compositional differences and correlations were identified in gahnite crystals from the studied pegmatites (Figs. 3, 9, 10).

Observed compositional differences are characterized by higher Zn and lower Fe contents in the rim compared to inner parts of the crystal (Figs. 3, 9, 10). Enrichment in Zn and depletion in Fe in the rim is only slightly seen in backscattered electron images as a somewhat patchy irregular rim (<300  $\mu\text{m}$  wide), but it is more marked as a very thin zone <50  $\mu\text{m}$  wide at the rim (Fig. 3F). A lower Fe and slightly higher Zn content within the crystal were also identified at points near fractures compared to other areas. Overall, for individual crystals analyzed in which consistent compositional variations were identified, Zn and  $\text{Fe}^{2+}$  show a moderate negative correlation ( $R^2 = 0.6$ ), and Zn and Mn do not show any correlation. Manganese exhibits a similar pattern to that of Fe, with a very small decrease towards the edge (<0.1 wt.% MnO), while the extremely low Mg content does not vary systematically from core to edge (Fig. 9). Relatively higher Zn and lower Fe contents in fractures and very thin rims are associated with muscovite growth, and are likely the result of a late process of fracturing and muscovite crystallization (Fig. 9).

The pattern of higher Zn and lower Fe contents near the rim compared to the core in some of the studied gahnite crystals is consistent with that identified

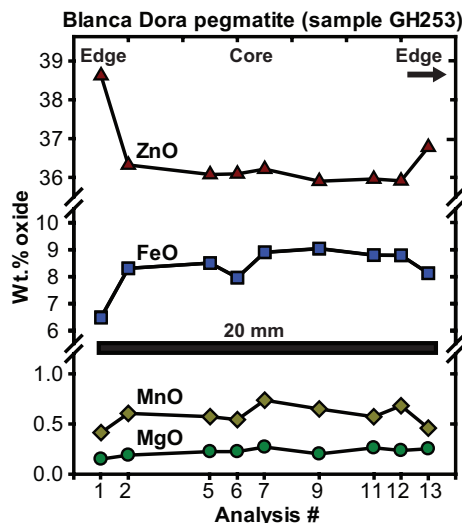


FIG. 9. Compositional profile across a gahnite crystal showing variations between the core and the edge. Blanca Dora pegmatite, Comechingones pegmatite district, sample GH253. Higher Zn and lower Fe and Mn contents are seen in the rim. Arrow below "Edge" indicates that the edge of the crystal is farther to the right. Point analysis with low Fe content within the crystal is located in or close to a fracture.

in gahnite from a granitic pegmatite in the Belvís de Monroy pluton in Spain (Merino *et al.* 2013). With the progression of pegmatite melt crystallization, the Fe content in the melt continually decreases while the Zn content increases, resulting in gahnite with higher Fe contents in the core than in the rim. This is also consistent with the information gained from the study of gahnite in granitic rocks that indicates that Zn is incompatible and stays in the melt until the crystallization of gahnite or other Zn-bearing minerals (Tulloch 1981). That late fluids have lower Fe and higher Zn contents than earlier ones, theoretically, suggests that the higher Zn and lower Fe contents towards the rim compared to inner parts of gahnite crystals from the Pampean Pegmatite Province reflect the evolution of fluids during pegmatite crystallization, independently of whether the chemical differences are due to early (primary) or late (fracturing and recrystallization) gahnite growth.

Other gahnite crystals show more complex compositional changes within the crystals, where the Zn, Fe, and Mn contents fluctuate, even though there is a small but marked increase in Zn and decrease in Fe at the edge of the crystal (Fig. 10). The many up and down fluctuations may be due to the high concentration of fractures, and many of the points analyzed lie near fractures. Even though the fluctuations also resemble oscillatory zoning recognized in other

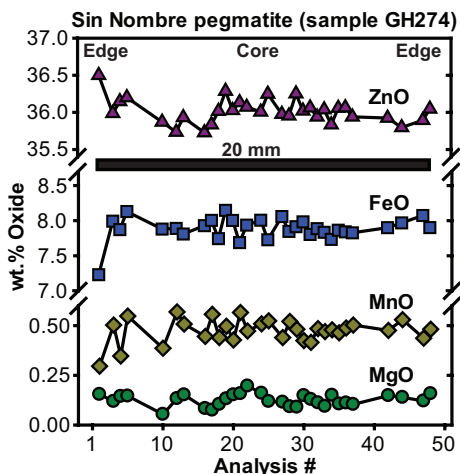


FIG. 10. Compositional profile across a gahnite crystal showing variations. Sin Nombre pegmatite, Comechingones pegmatite district, sample GH274A. Central region shows typical fluctuations seen in many crystals and an increase in Zn and decrease in Fe towards the edge.

minerals (*e.g.*, Lussier & Hawthorne 2011) due to their random nature and association with fractures, it is more likely that the chemical changes are related to a late process that shows the nature of fluid evolution at this stage. More detailed studies are required to decipher exactly how the more complex elemental variations originated and their significance, if any, for pegmatite melt evolution.

#### Comparison with gahnite in granitic pegmatites worldwide and MMSDs

In the ternary diagram in terms of the hercynite, gahnite, and spinel endmembers, the composition of gahnite in granitic pegmatites from Argentina falls within the field of gahnite in granitic pegmatites defined by Spry & Scott (1986a) (Fig. 11). Compositions of gahnite obtained in this study, along with other published data from granitic pegmatites worldwide, were used to redefine the compositional field of Zr-rich spinel in granitic pegmatites originally presented by Němec (1973) and improved by Spry & Scott (1986a) (Fig. 11). These gahnite compositions fall in the upper, Zn endmember portion of the spinel ternary diagram and are characterized by low Mg contents and a wide range of Zn and Fe values and defined by the following endmember variations:  $Ghn_{50-98}Hc_{1-50}Spl_{0-7}$ . It is worth noting that in a recent study, Merino *et al.* (2013) redefined the compositional field of gahnite in granitic pegmatites from Spry & Scott (1986a), but they referred to gahnite from igneous rocks, not just from granitic pegmatites. We have defined the field here to include only

the compositions of gahnite from granitic pegmatites. Considering that relatively high Zn and low Fe and Mg contents in gahnite reflect increasing melt evolution, the compositions of gahnite from the granitic pegmatites studied here reflect a low to intermediate degree of melt fractionation in comparison to gahnite from other granitic pegmatites worldwide (Fig. 11).

The new gahnite compositional field partially overlaps that of gahnite from metamorphosed massive sulfide deposits (MMSDs) in Fe-Al-rich metasedimentary and metavolcanic rocks, metabauxites, and unaltered and hydrothermally altered Fe-Al-rich metasedimentary and metavolcanic rocks, as defined by Heimann *et al.* (2005). Some gahnite from MMSDs have considerably higher Mg contents than gahnite from granitic pegmatites, but comparable percentages of Zn and Fe. Gahnite from unaltered and hydrothermally altered Fe-Al-rich metasedimentary and metavolcanic rocks may have similar Mg ranges as gahnite from granitic pegmatites but contain a more diverse range of Fe and Zn contents from nearly pure hercynite to pure gahnite. Unlike in these rocks, gahnite from metabauxites is constrained to the nearly

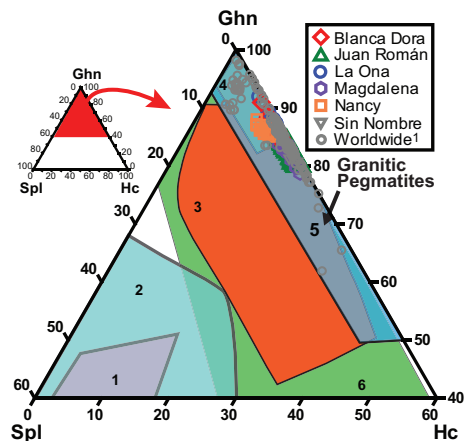


FIG. 11. Compositions of gahnite in granitic pegmatites from the Argentina pegmatites studied here and those in worldwide pegmatites reported in the literature expressed in terms of gahnite (Ghn), hercynite (Hc), and spinel (Spl) endmembers (mol.%) superimposed on the redefined spinel compositional field for granitic pegmatites. Field numbers: (1) marbles, (2) metamorphosed massive sulfide deposits and S-poor rocks in Mg-Ca-Al alteration zones, (3) metamorphosed massive sulfide deposits in Fe-Al-rich metasedimentary and metavolcanic rocks, (4) metabauxites, (5) granitic pegmatites, and (6) unaltered and hydrothermally altered Fe-Al-rich metasedimentary and metavolcanic rocks. The inset shows the top 60% of the diagram presented (gahnite endmember). Modified from Němec (1973), Spry & Scott (1986a), Heimann *et al.* (2005), and Merino *et al.* (2013). <sup>1</sup>References for data for gahnite in pegmatites worldwide from Table 3.

pure zinc endmember, ranging from 85 to 100 mol.% gahnite and with up to 7 mol.% spinel. Therefore, the typical characteristic of gahnite from granitic pegmatites is low Mg and Fe and high Zn contents, even though the extremes can also be found in other rock types. Trace element studies of gahnite may help define compositional differences among gahnite from various geologic settings, which could be used to estimate degrees of pegmatite fractionation.

### CONCLUSIONS

Based on the compilation of gahnite occurrences from previous studies, the conditions required to form gahnite in granitic pegmatite melts are most often met by peraluminous granitic pegmatites of the rare-element classes and LCT family. However, some granitic pegmatites of the muscovite-rare element class, such as the Burleson Mica Mine from Spruce Pine, also meet these requirements.

On the ternary diagram of spinel endmembers, gahnite in granitic pegmatites from the Comechingones pegmatite district and the Nancy pegmatite in the Conlara district in Argentina plots within the previously defined field for gahnite in granitic pegmatites with the following endmember ranges:  $\text{Ghn}_{75.9-86.6}\text{Hc}_{7.1-20.0}\text{Spl}_{0.24-3.19}\text{Gl}_{x0.66-2.26}\text{Mag}_{0-9.3}$ . In the plot of molecular  $(\text{Fe}^{2+} + \text{Mg})/\text{Al}$  versus  $(\text{Zn} + \text{Mn})/\text{Al}$ , gahnite compositions from the Argentina pegmatites studied here are similar to those from the LCT Separation Rapids pegmatites.

Based on  $\text{Fe}^{2+}$  versus Zn relations, the Sin Nombre, Magdalena, and Juan Román pegmatites are the least evolved pegmatites due to the lowest Zn contents and Zn/Fe<sup>2+</sup> ratios (>3.83) in gahnite, which is consistent with the mineralogical evidence. Gahnite in the La Ona pegmatite has the highest Zn/Fe<sup>2+</sup> ratios (<9.98) of the gahnite studied here and reflects the most evolved melt, also consistent with the mineralogy of the pegmatites. Gahnite from the Nancy pegmatite has high Zn/Fe<sup>2+</sup> ratios (<7.89) but higher Mg and Mn contents than gahnite from the Comechingones pegmatites, which, consistent with mineralogy, indicates a slightly lower degree of evolution compared with the latter.

A plot of molecular Zn versus  $(\text{Fe}^{2+} + \text{Mg} + \text{Mn})$  shows a very good linear correlation for gahnite from Argentina pegmatites as well as those from pegmatites worldwide, indicating that these parameters represent well the compositional variations in gahnite, and this is a useful diagram to investigate relative pegmatite melt evolution. A new diagram of molecular  $(\text{Fe} + \text{Mg})$  versus  $(\text{Zn} + \text{Mn})$  yields the best negative correlation for the gahnite compositions presented here, as well as those previously published, and best displays the substitutions in gahnite defined by increasing Zn + Mn and decreasing Fe + Mg with progressive melt evolution. Without implying a co-magmatic origin for the pegmatites, based on pegmatite mineralogy, Zn

contents, Zn/Fe<sup>2+</sup> ratios, and combined Zn + Mn and Fe + Mg in gahnite, the relative degree of evolution of the pegmatites increases in the order: Sin Nombre → Magdalena → Juan Román → Blanca Dora → Nancy → La Ona.

Gahnite from the studied pegmatites exhibits intracrystal compositional variations characterized by higher Zn (up to 2.7 wt.% ZnO) and lower Fe contents in zones near the edge compared to inner parts of the crystal, as well as near fractures filled with muscovite and near rims with muscovite. This compositional zoning reflects fluid evolution *via* fractional crystallization, and can also be related to a late-stage process of pegmatite crystallization associated with muscovite growth in fractures and rims of gahnite. It can, therefore, explain the evolution of fluids during early (primary) or late (fracturing and recrystallization) gahnite growth.

Based on a review of previously published compositions of gahnite from granitic pegmatites worldwide and the new data from Argentina presented here, the re-defined compositional field for gahnite in this type of rock in the spinel ternary diagram has the following ranges:  $\text{Ghn}_{50-98}\text{Hc}_{1-50}\text{Spl}_{0-7}$ . This compositional field partly overlaps those of gahnite from MMSDs in Fe-Al-rich metasedimentary and metavolcanic rocks, metabauxites, and unaltered and hydrothermally altered Fe-Al-rich metasedimentary and metavolcanic rocks. However, gahnite from MMSDs tends to reach higher Mg contents than gahnite from granitic pegmatites and the highest Zn contents are observed in gahnite from the latter. Gahnite from granitic pegmatites also overlaps the composition of metabauxites, but these are limited to almost pure gahnite.

This study shows that the major element composition of gahnite in granitic pegmatites can be used to determine the relative degree of evolution of pegmatite-forming melts. Detailed chemical studies combining major and trace elements in gahnite from granitic pegmatites may further our understanding of pegmatite melt evolution and major and trace element behavior in these felsic melts.

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## REFERENCES

- ADAMS, C.J., MILLER, H., ACEÑOLAZA, F.G., TOSELLI, A.J., & GRIFFIN, W.L. (2011) The Pacific Gondwana margin in the late Neoproterozoic-early Paleozoic: Detrital zircon U-Pb ages from metasediments in northwest Argentina reveal their maximum age, provenance and tectonic setting. *Gondwana Research* **19**, 71–83.
- ALFONSO, P. & MELGAREJO, J.C. (2008) Fluid evolution in the zoned rare-element pegmatite field at Cap de Creus, Catalonia, Spain. *Canadian Mineralogist* **46**, 597–617.
- ALFONSO, P., CORBELLA, M., & MELGAREJO, J.C. (1995) Nb-Ta-minerals from the Cap de Creus pegmatite field, eastern Pyrenees: distribution and geochemical trends. *Mineralogy and Petrology* **55**, 53–69.
- ALFONSO, P., MELGAREJO, J.C., YUSTA, I., & VELASCO, F. (2003) Geochemistry of feldspars and muscovite in granitic pegmatite from the Cap de Creus Field, Catalonia, Spain. *Canadian Mineralogist* **41**, 103–116.
- BATCHELOR, R. & KINNAIRD, J. (1984) Gahnite compositions compared. *Mineralogical Magazine* **48**, 425–429.
- ČERNÝ, P. & ERICIT, T.S. (2005) The classification of granitic pegmatites revisited. *Canadian Mineralogist* **43**, 2005–2026.
- ČERNÝ, P. & HAWTHORNE, F.C. (1982) Selected peraluminous minerals. *Mineralogical Association of Canada Short Course Handbook* **8**, 163–186.
- ČERNÝ, P., LONDON, D., & NOVÁK, M. (2012) Granitic pegmatites as reflections of their sources. *Elements* **8**, 289–294.
- CLARKE, D.B. (1981) The mineralogy of peraluminous granites: a review. *Canadian Mineralogist* **19**, 3–17.
- DANA, E.S. (1904) *The System of Mineralogy of James Dwight Dana. Descriptive Mineralogy*. Sixth Ed. New York, John Wiley & Sons.
- DEMARTIS, M., PINOTTI, L.P., D'ERAMO, F.J., CONIGLIO, J.E., & AGULLEIRO, L.A. (2010) Emplazamiento de pegmatitas graníticas del sector sur del distrito pegmatítico Comechingones, Córdoba. *Revista de la Asociación Geológica Argentina* **67**, 536–544.
- DEMARTIS, M., PINOTTI, L.P., CONIGLIO, J.E., D'ERAMO, F.J., TUBÍA, J.M., ARAGÓN, E., & AGULLEIRO, L.A. (2011) Ascent and emplacement of pegmatite melts in a major reverse shear zone (Sierras de Córdoba, Argentina). *Journal of Structural Geology* **33**, 1334–1346.
- DEMARTIS, M., ARAGÓN, E., CONIGLIO, J.E., PINOTTI, L.P., D'ERAMO, F.J., AGULLEIRO INSÚA, L.A., MAFFINI, M.N., & PETRELLI, H.A. (2012) Geoquímica y metalogénesis de las pegmatitas y granitos asociados del sector sur del distrito Comechingones, Córdoba. *Serie Correlación Geológica* **28(1)**, 103–116.
- DIAS, P.S.A. (2011) *Análise estrutural e paragenética de produtos litológicos e mineralizações de segregação metamórfica – Estudo de veios hiperaluminosos e protólitos poligénicos Silúricos da região da Serra de Arga (Minho)*. Ph.D Thesis, Universidade de Minho, Portugal, 615 p.
- DOMAŃSKA-SIUDA, J. (2007) The granitoid Variscan Strzegom-Sobótka massif. *Granitoids in Poland, AM Monograph* **1**, 179–191.
- DROBE, M., LÓPEZ DE LUCHI, M., STEENKEN, A., WEMMER, A., NAUMANN, R., FREI, R., & SIEGSMUND, S. (2011) Geodynamic evolution of the Eastern Sierras Pampeanas (Central Argentina) based on geochemical, Sm-Nd, Pb-Pb and SHRIMP data. *International Journal of Earth Science* **100**, 631–657.
- DRUGUET, E. & HUTTON, D.H.W. (1998) Syntectonic anatexis and magmatism in a mid-crustal transpressional shear zone: an example from the Hercynian rocks of the eastern Pyrenees. *Journal of Structural Geology* **20**, 905–916.
- DUNLOP, S.D. (2000) *Gahnite from metamorphosed massive sulphide deposits and rare-element pegmatites: Development of discriminators based on bedrock and overburden samples*. M.Sc. Thesis, Laurentian University, 169 p.
- ESKOLA, P. (1914) An occurrence of gahnite in pegmatite near Träskböle in Perniö, Finland. *Geologiska Föreningen i Stockholm Förhandlingar* **36**, 25–30.
- FETTES, D.J. & MENDUM, J.R. (1987) The evolution of the Lewisian complex in the Outer Hebride. *Geological Society of London Special Publications* **27**, 27–44.
- GALLISKI, M.A. (1994a) La Provincia Pegmatítica Pampeana. I: Tipología y distribución de sus distritos económicos. *Revista de la Asociación Geológica Argentina* **49**, 99–112.
- GALLISKI, M.A. (1994b) La Provincia Pegmatítica Pampeana. I: Metalogénesis de sus distritos económicos. *Revista de la Asociación Geológica Argentina* **49**, 113–122.
- GALLISKI, M.A. (1999a) Distrito pegmatítico Comechingones, Córdoba. In Recursos Minerales de la República Argentina (E.O. Zappettini, ed.). *Instituto de Geología y Recursos Minerales SEGEMAR* **35**, 361–364.
- GALLISKI, M.A. (1999b) Distrito pegmatítico Conlara, San Luis. In Recursos Minerales de la República Argentina (E.O. Zappettini, ed.). *Instituto de Geología y Recursos Minerales SEGEMAR* **35**, 365–368.

- GALLISKI, M.A. (2009) The Pampean Pegmatite Province, Argentina: a review. *Estudios Geológicos* **19**, 30–34.
- GALLISKI, M.A. & ČERNÝ, P. (2006) Geochemistry and structural state of columbite-group minerals in granitic pegmatites of the Pampean Ranges, Argentina. *Canadian Mineralogist* **44**, 645–666.
- GALLISKI, M.A. & LINARES, E. (1999) New K-Ar muscovite ages Form granitic pegmatites of the Pampean Pegmatite Province. *Actas II Segundo Simposio Sudamericano de Geología Isotópica*. Anales XXXIV SEGEMAR, 63–67.
- GALLISKI, M.A. & SFRAGULLA, J. (2014) Las pegmatitas graníticas de las sierras de Córdoba. *19th Congreso Geológico Argentino, Relatorio*, 365–388.
- GALLISKI, M.A., MÁRQUEZ-ZAVALÍA, M.F., MARTÍNEZ, V., & ROQUET, M.B. (2011) Granitic pegmatites of the San Luis Ranges. *5th International Symposium on Granitic Pegmatites, PEG2011 Argentina, Field Trip Guidebook: Ianipla-Conicet*, 44 p.
- GALLISKI, M.A., MÁRQUEZ-ZAVALÍA, M.F., LIRA, R., CEMPÍREK, J., & ŠKODA, R. (2012) Mineralogy and origin of the dumortierite-bearing pegmatites of Virorco, San Luis, Argentina. *The Canadian Mineralogist* **50**, 873–894.
- HANSON, S., SIMMONS, W.B., & FALSTER, A.U. (1998) Nb-Ta-Ti oxides in granitic pegmatites from the Topsham Pegmatite District, southern Maine. *Canadian Mineralogist* **36**, 601–608.
- HEIMANN, A., SPRY, P., & TEALE, G. (2005) Zincian spinel associated with metamorphosed Proterozoic base-metal sulfide occurrences, Colorado: A re-evaluation of gahnite composition as a guide in exploration. *Canadian Mineralogist* **43**, 601–622.
- HESS, P.C. (1989) *Origins of Igneous Rocks*. Cambridge, Harvard University Press, 336 p.
- HUB, C. (1994) Estudio geológico económico de pegmatitas del Distrito Comechingones. *Informe Beca CONICOR, Unpubl. Rep.*, Córdoba, 156 p.
- HUB, C. (1995) Estudio geológico económico de pegmatitas del Distrito Comechingones. *Informe Beca CONICOR, Unpubl. Rep.*, Córdoba, 172 p.
- HUHMA, H. (1986) Sm-Nd, U-Pb, and Pb-Pb isotopic evidence for the origin of the Early Proterozoic Sveckarelian crust in Finland. *Geological Survey of Finland, Bulletin* **337**, 52 p.
- JACKSON, B. (1982) Gem quality gahnite from Nigeria. *The journal of Gemmology and proceedings of the Gemological Association of Great Britain* **18**, 265–276.
- JANEČEK, J. (2007) Intragranitic pegmatites of the Strzegom-Sobótka massif - an overview. *Granitoids in Poland, AM Monograph* **1**, 193–201.
- JOHNSON, R.G. (1998) *Mineralogy and Geochemistry of the Lord Hill Pegmatite*. M.Sc. Thesis, University of New Orleans, New Orleans, Louisiana, 127 p.
- LEAL GOMES, C., CASTRO, P., & ALVES, C. (1995) Caracterização de espinelas ziníferas e do par ganite-nigerite no campo aplito-pegmatítico da Serra de Argamimho- N de Portugal. *Memórias 4, Publicações do Museu e Laboratório Mineralógico e Geológico, Universidade do Porto*, 629–633.
- LI, Z., ZHANG, W., YANG, R., LI, W., & ZHAI, W. (1999a) Analysis of chemical composition of melt inclusion of beryl in pegmatite and discovery of zinc-spinel by electronic probe. *Chinese Science Bulletin* **44**, 2004–2010.
- LI, Z., YANG, R., & LI, W. (1999b) Pegmatite fluids of different origins and their implications for mineralization. *Chinese Journal of Geochemistry* **18**, 9–17.
- LUSSIER, A.J. & HAWTHORNE, F.C. (2011) Oscillatory zoned liddicoatite from Anjanabonoina, central Madagascar. II. Compositional variation and mechanisms of substitution. *Canadian Mineralogist* **49**, 89–104.
- MERINO, E., VILLASECA, C., PÉREZ-SOBA, C., & OREJANA, D. (2010) First occurrence of gahnite and chrysoberyl in an Iberian Hercynian Pluton: the Belvís de Monroy Granite (NE Cáceres, Spain). *Sociedad Española de Mineralogía* **159**–160.
- MERINO, E., VILLASECA, C., OREJANA, D., & JEFFRIES, T. (2013) Gahnite, chrysoberyl and beryl co-occurrence as accessory minerals in a highly evolved peraluminous pluton: The Belvís de Monroy leucogranite (Cáceres, Spain). *Lithos* **179**, 137–156.
- MORRIS, T.F., BREAKS, F.W., AVERILL, S.A., CRABTREE, D.C., & McDONALD, A. (1997) Gahnite composition: Implications for base metal and rare-element exploration. *Exploration and Mining Geology* **6**, 253–260.
- MORTEANI, G., EICHINGER, F., GÖTZE, J., TARANTOLA, A., & MÜLLER, A. (2012) Evaluation of the potential of the pegmatite quartz veins of the Sierra de Comechingones (Argentina) as a source of high purity quartz by a combination of LA-ICP-MS, ICP, cathodoluminescence, gas chromatography, fluid inclusion analysis, Raman and FTIR spectroscopy. *In Quartz: Deposits, Mineralogy and Analytics* (J. Götze & R. Möckel, eds.). Berlin, Springer, (119–137).
- NEIVA, A.M.R. (2013) Micas, feldspars and columbite–tantalite minerals from the zoned granitic lepidolite-subtype pegmatite at Namivo, Alto Ligonha, Mozambique. *European Journal of Mineralogy* **25**, 967–985.
- NEIVA, A.M.R. & CHAMPNESS, P.E. (1997) Nigerite and gahnite from the granitic pegmatite veins of Cabanas, Ponte do Lima, northern Portugal. *Neues Jahrbuch Für Mineralogie - Monatshefte*, 1997, **9**, 384–409.
- NEIVA, A.M.R. & NEIVA, J.M.C. (2005) Beryl from the granitic pegmatite at Namivo, Alto Ligonha, Mozambique. *Neues Jahrbuch Für Mineralogie - Abhandlungen* **181**, 173–182.
- NEIVA, J.M.O., RIMSKY, A., & SANDRÉA, A. (1955) Sur une variété de gahnite stannifère de Cabanas (Portugal). *Bulletin de la Société Française de minéralogie et de cristallographie* **78**, 97–105.

- NĚMEC, D. (1973) Das Vorkommen der Zn-Spinelle in der Böhmischen Masse. *TMPM Tschermaks mineralogische und petrographische Mitteilungen* **19**, 95–109.
- O'BRIEN, J.J., SPRY, P.G., TEALE, G.S., JACKSON S.E., & ROGERS, D. (2014) Major and trace element chemistry of gahnite as an exploration guide to Broken Hill-type Pb-Zn-Ag mineralization in the Broken Hill Domain, New South Wales, Australia. *Economic Geology* **110**, 1027–1057.
- OTAMENDI, J.E., CASTELLARINI, P.A., FAGIANO, M.R., DEMICHELIS, A.H., & TIBALDI, A.M. (2004) Cambrian to Devonian geologic evolution of the Sierra de Comechingones, Eastern Sierra Pampeanas, Argentina: Evidence for the development and exhumation of continental crust on the Proto-Pacific margin of Gondwana. *Gondwana Research* **7**, 1143–1155.
- PALACHE, C., BERMAN, H., & FRONDEL, C. (1944) *Dana's System of Mineralogy*. 7<sup>th</sup> Edition, Volume I, 689–697.
- PEHRMAN, G. (1948) Gahnit von Rosendal auf Kimito, SW-Finland. *Bulletin of the Geological Institution of the University of Uppsala* **32**, 329–336.
- RINALDI, C.A. (1968) Estudio de las pegmatitas uraníferas de las Sierras de Comechingones, Provincia de Córdoba. *Revista de la Asociación Geológica Argentina* **23(3)**, 161–195.
- SCHWARTZ, J.J., GROMET, L.P., & MIRÓ, R. (2008) Timing and duration of the calc-alkaline arc of the Pampean Orogeny: Implications for the Neoproterozoic to Cambrian evolution of western Gondwana. *The Journal of Geology* **116**, 39–61.
- SIEGESMUND, S., STEENKEN, A., MERTINO, R., WEMMER, K., LÓPEZ DE LUCHI, M., FREI, R., PRESNYAKOV, S., & GUERESCHI, A. (2010) Time constraints on the tectonic evolution of the Eastern Sierras Pampeanas (Central Argentina). *International Journal of Earth Sciences* **99**, 1199–1226.
- SIMS, J.P., IRELAND, T.R., CAMACHO, A., LYONS, P., PIETERS, P.E., SKIRROW, R.G., STUART-SMITH, P.G., & MIRÓ, R. (1998) U-Pb, Th-Pb, and Ar-Ar geochronology from the southern Sierras Pampeanas, Argentina: implications for the Palaeozoic tectonic evolution of the western Gondwana margin: The Proto-Andean Margin of Gondwana. *Geological Society of London Special Publications* **142**, 259–281.
- SOARES, D.R., BEURLEN, H., FERREIRA, A.C.M., & DA-SILVA, M.R.R. (2007) Chemical composition of gahnite and degree of pegmatite fractionation in the Borborema Pegmatite Province, northeastern Brazil. *Anais da Academia Brasileira de Ciências* **79**, 395–404.
- SOARES, D.R., BEURLEN, H., DE BRITO BARRETO, S., SILVA, M. R.R., & FERREIRA, A.C.M. (2008) Compositional variation of tourmaline-group minerals in the Borborema Pegmatite Province, northeastern Brazil. *Canadian Mineralogist* **46**, 1097–1116.
- SPRY, P.G. (1987) Compositional zoning in zincian spinel. *Canadian Mineralogist* **25**, 97–104.
- SPRY, P.G. & SCOTT, S.D. (1986a) The stability of zincian spinels in sulfide systems and their potential as exploration guides for metamorphosed massive sulfide deposits. *Economic Geology* **81** 1446–1463.
- SPRY, P.G. & SCOTT, S.D. (1986b) Zincian spinel and staurolite as guides to ore in the Appalachians and Scandinavian Caledonides. *Canadian Mineralogist* **24** 147–163.
- STEENKEN, A., WEMMER, K., LÓPEZ DE LUCHI, M., SIEGESMUND, S., & PAWLIG, S. (2004) Crustal provenance and cooling of the basement complexes of the Sierra de San Luis: An insight into the tectonic history of the Proto-Andean margin of Gondwana. *Gondwana Research* **7**, 1171–1195.
- STEENKEN, A., LÓPEZ DE LUCHI, M.G., MARTINO, R.D., SIEGESMUND, S., & WEMMER, K. (2005) SHRIMP dating of the El Peñón granite: a time marker at the turning point between the Pampean and Famatinian cycles within the Conlara Metamorphic Complex (Sierra de San Luis; Argentina)? 16th Congreso Geológico Argentino. *Actas* **1**, 889–896.
- STEENKEN, A., SIEGESMUND, S., LÓPEZ DE LUCHI, M., FREI, R., & WEMMER, K. (2006) Neoproterozoic to Early Palaeozoic events in the Sierra de San Luis: implications for the Famatinian geodynamics in the Eastern Sierras Pampeanas (Argentina). *Journal of the Geological Society of London* **163**, 965–982.
- STEENKEN, A., SIEGESMUND, S., WEMMER, K., & LÓPEZ DE LUCHI, M. (2008) Time constraints on the Famatinian and Achalian structural evolution of the basement of the Sierra de San Luis (Eastern Sierras Pampeanas, Argentina). *Journal of South American Earth Sciences* **28**, 336–358.
- STEENKEN, A., WEMMER, K., MARTINO R.D., LÓPEZ DE LUCHI, M., GUERESCHI, A., & SIEGESMUND, S. (2010) Post-Pampean cooling and the uplift of the Sierras Pampeanas in the west of Córdoba (Central Argentina). *Neues Jahrbuch für Geologie und Paläontologie-Abhandlungen* **256(2)**, 235–255.
- SWANSON, S.E. & VEAL, W.B. (2010) Mineralogy and petrogenesis of pegmatites in the Spruce Pine District, North Carolina, USA. *Journal of Geosciences* **55**, 27–42.
- SZUSZKIEWICZ, A. & ŁOBOS, K. (2004) Gahnite from Siedlimowice, Strzegom-Sobótka granitic massif, SW Poland. *Mineralogia Polonica* **35**, 15–21.
- TAIT, K.T., HAWTHORNE, F.C., ČERNÝ, P., & GALLISKI, M.A. (2004) Bobfergusonite from the Nancy Pegmatite, San Luis Range, Argentina: Crystal-structure refinement and chemical composition. *Canadian Mineralogist* **42**, 705–716.
- TINDLE, A.G. & BREAKS, F.W. (1998) Oxide minerals of the Separation Rapids rare-element granitic pegmatite group, northwestern Ontario. *Canadian Mineralogist* **36**, 609–635.

- TULLOCH, A.J. (1981) Gahnite and columbite in an alkali-feldspar granite from New Zealand. *Mineralogical Magazine* **44**, 275–278.
- TURNIAK, K., HALAS, S., & WÓJTOWICZ, A. (2007) New K-Ar cooling ages of granitoids from the Strzegom-Sobótka Massif, SW Poland. *Geochronometria* **27**, 5–9.
- VON GOSEN, W. & PROZZI, C. (1998) Structural evolution of the Sierra de San Luis (Eastern Sierras Pampeanas, Argentina): implications for the Proto-Andean Margin of Gondwana. In *The Proto-Andean Margin of Gondwana* (R.J. Pankhurst & C.W. Rapela, eds.). *Geological Society of London Special Publications* **142**, 235–258.
- VON KNORRING, O. & DEARNLEY, R. (1960) The Lewisian pegmatites of South Harris, Outer Hebrides. *Mineralogical Magazine* **32**, 366–378.
- WHITNEY, D.L. & EVANS, B.W. (2010) Abbreviations for names of rock-forming minerals. *American Mineralogist* **95**, 185–187.
- WINDLEY, B.F., KRÖNER, A., GUO, J., QU, G., LI, Y., & ZHANG, C. (2002) Neoproterozoic to Paleozoic geology of the Altai Orogen, NW China: New zircon age data and tectonic evolution. *Journal of Geology* **110**, 719–737.
- WISE, M. & FRANCIS, C. (1992) Distribution, classification and geological setting of granitic pegmatites in Maine. *Northeastern Geology* **14**, 82–93.
- ZHU, Y., ZENG, Y., & GU, Y. (2006) Geochemistry of the rare-metal-bearing pegmatite No. 3 vein and related granites in the Keketuohai region, Altay Mountains, northwest China. *Journal of Asian Earth Sciences* **27**, 61–77.
- ZIMMERMAN, U. (2005) Terrane processes at the margins of Gondwana. *Geological Society of London Special Publications* **246**, 381–416.

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