**Internal framework and geochemistry of the Carboniferous Huaco granite pluton, Sierra de Velasco, NW Argentina**

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**ABSTRACT.** The A-type Huaco granite pluton of the Velasco range (Sierras Pampeanas of northwest Argentina) is formed by three coeval granitic facies and contains subordinate coeval-to-late facies, as well as enclaves, dikes and stocks that show different temporal relations, textures and compositions. The dominant facies (Regional Porphyritic Granite; RPG) is a porphyritic two-mica monzo- to syenogranite, with abundant microcline megacrysts up to 12 cm in size. It was emplaced in a dominant extensional setting and has a mainly crustal source but with participation of a mantle-derived component. The RPG transitions towards two coeval and co-genetic granite facies, at its margins (Border Granite; BG) and around Be-pegmatites (Adjacent Porphyritic Granite; APG). These two facies have a finer-grained texture and smaller and less abundant megacrysts. They are also monzo- to syenogranites, but a slight decrease in the biotite/muscovite ratio is observed from the BG to the RPG to the APG. Trace element modeling suggests that the RPG, BG and APG differentiated from the same magma source by fractional crystallization. Temporally older mafic (ME) and felsic (FE) enclaves are common in the pluton. The ME can be considered partially assimilated remnants of a mafic component in the genesis of the RPG, whereas the FE seem to be remnants of premature aplites. Other subordinate rocks intrude the RPG and are, hence, temporally younger: felsic dikes (FD), dioritic dikes (DD) and equiganular granites (EqG) are clearly posterior, whereas coeval-to-late Be-pegmatites (BeP) and orbicular granites (OG) formed during the final stages of crystallization of the pluton. The BeP, OG and FD indicate the presence of abundant water and volatiles. The EqG form small stocks that intrude the RPG and were possibly originated from purely crustal sources. The DD probably correspond to a younger unrelated episode of mafic magmatism.

**Keywords:** Granitic facies, REE and LIL composition, Fractional crystallization model, Huaco granite, Velasco range, Sierras Pampeanas.

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**RESUMEN. Estructura interna y geoquímica del plutón granítico carbonífero de Huaco, Sierra de Velasco, NW de Argentina.** El Plutón Huaco, ubicado en la sierra de Velasco (en Sierras Pampeanas del noroeste de Argentina), es de afinidad granítica A y está conformado por tres facies graníticas y contiene varias rocas ígneas subordinadas, las que muestran diferentes relaciones temporales, texturas y composiciones. Las facies granítica dominante (Granito Porfirico Regional; RPG) es un monzo-sienogranito de dos micas, de textura porfírica con abundantes megacristales de microclino que pueden alcanzar hasta 12 cm de longitud. Ha sido emplazado en un marco tectónico dominantemente extensional y habría tenido una fuente de origen cortical pero también con participación de componentes mantélicos. En los bordes del Plutón Huaco y envolviendo a pegmatitas de berilo contenidas en el mismo (BeP), se reconocen las facies cogenéticas BG y APG respectivamente, las cuales tienen contacto transicional con el RPG. Estas dos facies tienen textura de grano...
1. Introduction

Granitic plutons usually display compositional and/or textural heterogeneities at different scales and magnitudes, which are commonly referred to as internal “facies”. Besides, temporally previous/early and/or posterior/later magmatic rocks are commonly included within the main or dominant granitic facies. In the field, these subordinate rocks are found as dikes, enclaves, small stocks, pegmatites, lenses or pods, or irregular bodies of varying dimensions, with either sharp or diffuse contacts with the main granitic facies. The study of these subordinate rocks and their relationships with the main granitic facies can give insights into the processes that formed the pluton and its magmatic evolution (e.g., Smith et al., 1999; Breiter et al., 2005; Černý et al., 2005).

An example of such plutons with a varied internal framework is the Lower Carboniferous Huaco Pluton, part of the Velasco Range in the Sierras Pampeanas of NW Argentina. It is formed predominantly of porphyritic syeno- to monzogranites and contains several distinct subordinate facies and associated magmatic rocks with variable morphologies, compositions, textures and temporal relations. Several previous studies have described the main features of this pluton and some of its minor facies (Grosse and Sardi, 2005; Grosse et al., 2009; Sardi et al., 2010, 2011; Dahlquist et al., 2010, 2013) as well as some of the associated rocks, for example, Be-pegmatites (Cravero, 2005; Sardi et al., 2015), an orbicular granite (Quartino and Villar Fabre, 1962; Grosse et al., 2010) and the La Chinchilla stock (Grosse et al., 2005, 2009; Macchioli Grande et al., 2015). However, none of these previous studies have considered all of the facies and associated magmatic rocks and their temporal and genetic links. In this paper, we revise and present new field, petrographic and geochemical data for each of the facies and related magmatic rocks of the Huaco pluton, in order to determine their distinctive features and deduce the genetic links among them.

2. Geology of the Velasco Range

The Velasco range, located in La Rioja province of NW Argentina (Fig. 1a), is one of the largest ranges of the Sierras Pampeanas geologic province, which is characterized by extensive outcrops of crystalline basement composed of Upper Precambrian to Ordovician metamorphic rocks (e.g., Rossi et al., 2002; Larrovere et al., 2011) and Ordovician to Lower Carboniferous igneous, mainly granitoid, rocks (e.g., Toselli et al., 1986, 2002; Rapela et al., 2001; Dahlquist et al., 2010, 2013; Alasino et al., 2012).

The Velasco range is formed essentially by granitoids (Grosse et al., 2003, 2011; Báez et al., 2005; Toselli et al., 2005, 2006). Only a small portion of the range is occupied by outcrops of low to high grade metamorphic rocks, which are recognized as the La Cebila Formation (González Bonorino, 1951) and more recently as the La Cebila Metamorphic Complex (LCMC; Verdecchia, 2009), of Early (-Middle) Ordovician age (Verdecchia et al., 2007, 2011) (Fig. 1b). The metamorphic rocks consist of a sequence of phylites, meta-quartzites, and minor micaceous and quartz-micaceous schists, gneiss and migmatites (Verdecchia and Baldo, 2010; De Los Hoyos et al., 2011; Larrovere et al., 2012).
Two pulses of magmatism are found in the Velasco range, Ordovician and Lower Carboniferous (Pankhurst et al., 2000; Toselli et al., 2007; Dahlquist et al., 2013). The Ordovician magmatic episode, linked to the Famatinian magmatic arc (e.g., Pankhurst et al., 1998), originated peraluminous S-type porphyritic granitoids on the northwestern and western flanks of the Velasco range, and metaluminous to weakly peraluminous I-type granodiorites and tonalites on the southern portion of the range (Bellos, 2005; Rossi et al., 2005a; Grosse et al., 2011; Bellos et al., 2015). The Ordovician granitoids were affected by dynamic metamorphism that generated NNW-SSE-trending ductile shear zones of regional extension. Shear zones dated at neighboring ranges constrain the timing of deformation to the Silurian-Early Devonian (e.g., Höckenreiner et al., 2003) (Fig. 1a).

The Lower Carboniferous magmatic episode produced post-tectonic granites that intrude the deformed Ordovician granitoids and metamorphic rocks of the LCMC. In the northern part of the range, the Asha and Santa Cruz granites have yielded ages of 361±4 and 354±4 Ma (U-Pb on monazite; Toselli et al., 2011), whereas the San Blas pluton has yielded an age of 340±3 Ma (U-Pb on zircon, SHRIMP, Dahlquist et al., 2006). In the central part of the range (Fig. 1b), the Huaco and Sanagasta granites have yielded ages of 350 to 358 Ma and 353±1 Ma, respectively (U-Pb on monazite; Grosse et al., 2009).
3. Huaco Granite Pluton

The sub-ellipsoidal (~40x30 km) Huaco granite pluton occupies an area of around 620 km² in the central-eastern part of the Velasco range (Fig. 1a, b). It is formed predominantly by two-mica porphyritic syeno- to monzogranites (Huaco granite s.l.; Grosse and Sardi, 2005; Grosse et al., 2009). It is in contact to the SW with another Lower Carboniferous pluton, the Sanagasta granite pluton (Grosse et al., 2009) (Fig. 1b).

Grosse et al. (2009) determined that the main facies of the Huaco granite is silica- and potassium-rich, ferroan, alkali-calcic to slightly calc-alkalic, and moderately to weakly peraluminous (ASI: 1.06-1.18). Furthermore, Grosse et al. (2009) concluded, based on isotopic data, that the Huaco granite has a mainly crustal source, but with some participation of a more primitive, possibly mantle-derived, component. The Huaco granite pluton has several characteristics indicating it is an A-type granite (e.g., Collins et al., 1982; Whalen et al., 1987; Eby, 1990, 1992): ferrous affinity (high Fe/Mg ratios), low CaO, Sr and Ba contents, high contents in trace elements such as Ga, Nb, Ta, Y and HREE, and high FeO/MgO ratios (Abdel Rahman, 1994) and F and Cl contents (Muñoz, 1984) in biotites (Grosse, 2007; Grosse et al., 2009; Dahlquist et al., 2010). However, the geochemical composition of the pluton is more compatible with a post-orogenic environment than with an anorogenic environment (Grosse, 2007; Grosse et al., 2009).

Both the Huaco and Sanagasta granites are host to the Be-pegmatites of the Velasco Pegmatitic District (Sardi et al., 2002, 2015). The geochemical evolutionary trend from the main facies of the Huaco granite towards the Be-pegmatites has been studied by Sardi et al. (2010, 2011). The Huaco granite consists of several facies and associated rocks which are described in the next section.

4. Internal Lithological Framework of the Huaco Granite Pluton

4.1. Occurrence and Petrography

The Huaco granite pluton is composed of a main and dominant porphyritic facies, previously studied by several authors (see above). Following Sardi et al. (2010), we name the main facies Regional Porphyritic Granite (RPG). This main facies transitions towards two coeval facies, at the margins of the pluton (Border Granite; BG) and around Be-pegmatites (Adjacent porphyritic granite; APG) (Figs. 1c and 2a). Two more facies found within the main RPG can be considered as coeval-to-late facies (Fig. 1b, c and a): Be-pegmatites (BeP) and an orbicular granite pod (OG).

In addition, other magmatic rocks are included in the Huaco granite pluton and can be temporally identified as early or posterior units spatially related to the main facies (RPG). The former are enclaves of either mafic (Mafic Enclaves; ME) or felsic compositions (Felsic Enclaves; FE), whereas the posterior rocks are mafic dikes (Dioritic Dikes; DD), felsic dikes (Felsic Dikes; FD) and equigranular leucogranite intrusive stocks (Equigranular Granites; EqG), including the La Chinchilla stock (Figs. 1b and 2b).

4.1.1. The main facies (RPG)

Regional Porphyritic Granite (RPG): it consists of syeno- to monzogranites with a porphyritic texture resulting from abundant idiomorphic microcline megacrysts immersed in a medium to coarse grained equigranular groundmass (Fig. 3a). The megacrysts reach sizes of up to 12 cm and their abundance varies between 24 and 39%. The mineralogy is quartz (25-39%), usually twinned plagioclase (18-31%), twinned and often perthitic microcline (19-33%), biotite (5-7%) and muscovite (2-6%), idiomorphic apatite (up to 0.5%) and zircon, monazite, opaque minerals, and occasionally fluorite (<1%) (Grosse et al., 2009).

4.1.2. The coeval facies (BG and APG)

These facies have been studied previously by Sardi et al. (2010 and 2011). They include:

Border Granite (BG): this is the marginal facies of the RPG and occurs in the northern and eastern margins of the Huaco granite pluton (Fig. 1b). It is approximately 100 m wide and grades transitionally towards the RPG (Fig. 2a). The BG is characterized by a finer-grained groundmass and smaller and less abundant megacrysts compared to the RPG (Fig. 3b). Its mineralogy is quartz (34-40%), twinned and zoned plagioclase (23-34%), twinned and perthitic microcline (19-33%), biotite (5-7%) and muscovite (2-4%). Apatite, zircon and opaque minerals are usually included in biotite (Sardi et al., 2011).
Adjacent Porphyritic Granite (APG): this facies surrounds the Be-pegmatites for distances not greater than 6 m from the pegmatite margins (Fig. 2a). Similar to the BG, the APG also has a finer-grained groundmass and less abundant (average value ~29%) and smaller (<4 cm) microcline megacrysts compared to the RPG (Fig. 3c). Also, it has higher quartz (28-56%) and microcline (26-52%) contents and less plagioclase (10-24%). A slight increase of muscovite and a decrease of biotite are also observed. Minor phases are apatite, zircon, monazite, and occasionally fluorite.

4.1.3. The coeval-to-late facies (BeP and OG)

Be-pegmatites (BeP): they are lens-shaped with the main axis length up to 140 m (Sardi et al., 2015).
They are commonly zoned, showing an aplitic or leucogranitic border zone, an intermediate pegmatitic zone composed mainly of K-feldspar and accessory minerals (beryl, apatite, triplite and muscovite), and a quartz core. The outer thin rim of the Be-pegmatites (Marginal Aplite of the Pegmatites, or MA, following Sardi et al., 2010) is in sharp contact with the APG and usually grades inward towards the Be-pegmatite zone. It commonly consists of aplites or more rarely of muscovite-rich equigranular leucogranites. The width of the MA is variable, but not greater than 0.8 m. Its mineralogy is quartz (35-44%), perthitic microcline and twinned plagioclase in similar amounts (16-27% and 19-33%, respectively); muscovite (≤10%) is the main accessory mineral, whereas biotite is scarce and sometimes absent; fluorite is recognized occasionally (around 1%). Columbite-tantalite is occasionally found (Sardi et al., 2015).

**Orbicular Granite (OG):** It is a small (65x15 m), irregularly shaped body located in the central part of the Huaco pluton (Fig. 1b). It has been studied by Quartino and Villar Fabre (1962) and Grosse et al. (2010). The OG consists of ellipsoid-shaped orbicules of 3 to 15 cm immersed in an aplitic-pegmatitic matrix. The orbicules consist of a core formed by a K-feldspar megacryst, partially to totally replaced by plagioclase, and alternating layers of radial and plume plagioclase crystals and tangentially oriented biotite rings (Grosse et al., 2010). Grosse et al. (2010) conclude that the orbicular granitoid formed in situ in a pocket of evolved and volatile-rich melt segregated from the surrounding partially crystallized Huaco granite, possibly via a filter pressing mechanism.

**4.1.4. Enclaves (ME and FE)**

**Mafic Enclaves (ME):** They are dark and small, with sizes mostly under 20 cm (Fig. 4a), and rarely up to 50 cm. They usually have rounded and oval shapes, occasionally being very stretched-out parallel...
to the magmatic flow. The contact with the host RPG is sharp. They commonly contain xenocrysts and xeno-megacrysts probably incorporated from the host granite magma (Fig. 4a and b).

The ME have predominantly tonalite compositions and fine-grained equigranular textures (0.1 to 0.5 mm). They are very rich in biotite, varying in abundance from 10% to 50%. Apatite is relatively abundant and is found as elongated prisms and needles included mostly in quartz and plagioclase. The content of opaque minerals is roughly proportional to the abundance of biotite and ranges from ~1% to 10%; pyrite, ilmenite and magnetite have been identified.

**Felsic Enclaves (FE):** these enclaves can reach 2 m in size. They have irregular or oval shapes and rounded borders (Fig. 4c), or more rarely straight sides (Fig. 4d). They are gray to light pink with equigranular textures, either fine-grained (0.3-1.5 mm) or fine-to-medium-grained (0.7-5.0 mm). Commonly, the microcline megacrystals of the RPG accumulate around the FE (Fig. 4c, d), suggesting an early formation for the enclaves.

Felsic enclaves are syenogranites with quartz (33-34%) and perthitic microcline (41-45%). Both minerals are xenomorphic. Plagioclase (15-19%) is found as small subidiomorphic twinned crystals. Muscovite is the main accessory mineral (5-7%) while biotite is scarce (<2%). Apatite and zircon are very scarce and are included in biotite.

**4.1.5. Dikes (DD and FD)**

**Dioritic Dikes (DD):** according to field observations of Grosse (2007) and Dahlquist et al. (2010), the Huaco granite pluton is cut by scarce dioritic dikes. They are black, fine grained (0.1-0.3 mm), up to 3 m wide and are in sharp contact with the RPG. Twinned sub-idiomorphic plagioclase is the most abundant mineral, commonly altered to sericite. Mafic minerals are found in an abundance of 20 to 30%. Biotite is the most abundant of them and it is found as subhedral sheets with typical pleocroism, generally altered to chlorite. Other mafic minerals present are hornblende, titanite and opaque minerals. Apatite forms small elongated prisms and needles, although in smaller abundances than in mafic enclaves. Secondary calcite is also observed.

**Felsic Dikes (FD):** they are usually straight and are in sharp contact with the RPG (Fig. 5a and b). They are aplitic (20-30 cm in width), (Fig. 5a) with a fine-grained equigranular texture (0.1 to 1.5 mm), although one slightly porphyritic leucogranitic dike was found (<2 m in width) (Fig. 5b). They are monzogranitic, with quartz (31%), microcline (28-32%) and plagioclase (27-35%) as essential minerals, and muscovite (6-10%) as the main accessory mineral; biotite is very scarce (<1%).

The leucogranitic dike contains small microcline megacrysts (size ~1.3 cm; proportion ~10%) immersed in a medium to fine-grained equigranular matrix. The modal composition is quartz (46%), microcline (29%), plagioclase (19%), biotite and muscovite (<2%). Garnet (~4%) has been identified in this dike; it is idiomorphic, with variable sizes from small crystals to 2.5 mm.

**4.1.6. Equigranular granites (EqG)**

**Equigranular Granites (EqG):** the EqG (Fig. 5c) are small bodies or stocks that intrude the RPG (Fig. 5d). Their sizes vary from very small (<100 m diameter) to larger stocks of more than 1 km². They have irregular shapes and usually sharp contacts (Fig. 5e).

The EqG are felsic two-mica monzogranites (muscovite>biotite). The quartz and microcline crystals have similar sizes, between 1-3 mm. Quartz (26-43%) form xenomorphic crystals. Plagioclase (25-35%) has sub-idiomorphic habit and polysynthetic twinning. Microcline (23-29%) is xenomorphic and twinned after pericline-albite law. Muscovite (2-9%) is generally more abundant than biotite (1-5%). Tourmaline is found in abundances of up to 1% in some EqG bodies. Apatite, zircon and monazite are very scarce.

The La Chinchilla stock (Fig. 1b) is a particular EqG that has received special attention because of its high U content (Grosse et al., 2005, 2009; Salvatore et al., 2011, 2013; Parra et al., 2011; Morello and Aparicio González, 2013). It is a medium-grained equigranular to slightly porphyritic leucogranite (Grosse et al., 2005, 2006 and 2009) that clearly intrudes the RPG. Its mineralogy consists of quartz, plagioclase, K-feldspar, biotite, fluorite, zircon, monazite, occasional beryl and very scarce apatite.

**4.2. Geochemistry**

Geochemical analysis is based on 35 representative samples of the different facies of the Huaco granite pluton and associated magmatic rocks: 8 of the
RPG; 2 of the BG; 7 of the APG; 4 of the MA; 6 of the ME; 3 of the FE; 1 of the DD; 2 of the FD and 2 of the EqG. The analyses were performed at the laboratories of IGME (Instituto Geominero de España), Naruto University of Education (Japan), Huelva University (Spain) and ACTLAB (Canada). Major elements were determined by XRF, and trace elements by ICP-MS/AES. The analyses are shown in table 1, and include our new data (*n*=8) together with previously unpublished analyses of Grosse (2007; *n*=7) and published data of both Grosse *et al.* (2009; *n*=5) and Sardi *et al.* (2010; *n*=15).

4.2.1. Major elements and Rb, Sr, Ba and Cs compositions

**Granitoids:** the facies and associated rocks of granitic composition are silica-rich, with SiO₂ mostly between 68 and 75%; two samples with higher contents of 78 and 81% belong to FD and MA, respectively. All rocks are peraluminous (ASI >1, average 1.16). The FeO₂ and TiO₂ contents are higher in the main and coeval facies (RPG, BG and APG) (FeO₂ >1.7%; TiO₂ ≥0.20%) than in the other rocks (FeO₂ <1.7% and TiO₂ ≤0.20%). This distinction is not so evident for MgO, as the 2 EqG and the 2 FE samples are within the range of the main and coeval facies. K₂O > Na₂O for all cases except for two MA samples. K₂O+Na₂O is between 7.4 and 9.4% for the RPG, APG and BG facies, between 5.6 and 8.4% for the MA, and between 8.4 and 9% for the other rocks.

All samples are rich in FeO in relation to MgO, with FeO/FeO₂+MgO ratios >0.79 (wt%) (Fig. 6a). Most samples plot in the ferroan field of “A-type granites” in the diagram of Frost *et al.* (2001) (Fig. 6a).
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* Sardi et al. / Andean Geology 45 (2): 229-248, 2018
| Sample | Y    | La   | Ce   | Pr   | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Yb   | Lu   | LREE | HREE | Eu/Eu* | La/Yb* |
|--------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|----------------------------------|
| 6587   | 65.0 | 47.4 | 107  | 12.8 | 45.8 | 10.9 | 0.82 | 9.54 | 1.95 | 12.0 | 2.25 | 5.99 | 0.97 | 5.58 | 0.74 | 225   | 39.0  | 0.25  | 5.68  |
| 6590   | 38.0 | 30.0 | 86.0 | 8.27 | 29.6 | 6.98 | 0.73 | 6.23 | 1.28 | 7.36 | 1.23 | 2.96 | 0.44 | 2.57 | 0.33 | 162   | 22.4  | 0.34  | 7.81  |
| 6591   | 105  | 48.3 | 14.7 | 28.4 | 37.4 | 15.0 | 0.94 | 1.00 | 2.84 | 2.75 | 1.92 | 2.04 | 0.39 | 2.21 | 0.38 | 124   | 26.4  | 0.37  | 7.72  |
| 6592   | 16.6 | 21.2 | 7.8  | 2.34 | 1.01 | 0.42 | 0.07 | 0.16 | 0.19 | 0.39 | 0.13 | 0.39 | 0.08 | 0.39 | 0.08 | 1.25  | 0.20  | 0.06  | 0.13  |

**nd:** not determined; *data from Sardi et al. (2010); °data from Grosse et al. (2009).
**°°data only Y from Sardi et al. (2010).**

Major elements in wt% and trace elements in ppm. ACNK Alumina saturation index.
in agreement with Grosse et al. (2009) and Dahlquist et al. (2010). In the diagram of Dall'Agno and Oliveira (2007) (Fig. 6b) the samples plot in both the “reduced” and “oxidized” A-type granite fields.

Regarding trace element contents, the rocks show both differences and similarities. In the case of Cs, the lowest values are in samples of the FD and FE (~4 and ~12 ppm, respectively), and the highest ones in samples of the EqG and APG (~115 ppm). Lower Rb contents (<300 ppm) are recorded in the BG facies and in one sample of the FD, while the highest content corresponds to a sample of the APG (658 ppm). Roughly, Ba and Sr contents gradually increase in the following sequence: MA, FD, FE, EqG, APG, RGP, BG. The BG facies contains the lowest Rb/Sr (3.6 and 3.8) and highest Ba/Rb (0.95 and 1.27) ratios, whereas the MA contains the highest (17.4-47.0) and lowest (0.09-0.19) ratios, respectively.

Finally, the La Chinchilla stock is very rich in SiO$_2$, weakly peraluminous, has very low Ca, P, Fe and Mg contents, and is strongly enriched in several trace elements, particularly Li, Rb, Nb, Ta, U, Th, Y and HREE (Grosse et al., 2009). Grosse et al. (2009), based on Nd isotopes, suggest that the La Chinchilla stock derived from a different, more primitive source compared to the Huaco granite; we do not consider it further in this study.

**ME and DD:** The 6 analyzed mafic enclaves have variable compositions that can be attributed to different degrees of assimilation and hybridization with the host rock. Three samples have low SiO$_2$ contents (<57%) and can be considered slightly assimilated by the granite magma, whereas one of them contains 70% SiO$_2$, similar to the host granite.

The ME samples have very high concentrations in FeOt and MgO and their abundances are inversely proportional to the SiO$_2$ content. They are also rich in CaO and P$_2$O$_5$. The alkali contents do not vary with SiO$_2$. The FeO/FeOt+MgO ratios in the ME are variable between 0.69 and 0.86.

The dioritic dike (DD) shows evidence of assimilation of felsic material. The analyzed sample has a low SiO$_2$ content (56.6%), similar to the less assimilated mafic enclaves. It presents high contents of ferromagnesian elements, CaO, alkalis and P$_2$O$_5$. Compared to the less assimilated mafic enclaves, it is poor in FeOt and rich in MgO, so its FeO/FeOt+MgO ratio is very low (0.68). The ASI of the DD is 0.84. On the other hand, the DD has a composition that is very similar to mafic dikes hosted in the Carboniferous San Blas granite in the north of the Velasco range (Báez, 2006).

The Cs (37-175 ppm), Rb (220-2758 ppm), Ba (118-189 ppm) and Sr (26-121 ppm) contents in the mafic enclaves (ME) are variable, whereas the DD has values of 28 ppm, 131 ppm, 222 ppm and 477 ppm, respectively.

**4.2.2. REE and Y composition**

Y content is greater in the RPG and APG than in all other granitoid rocks, but the values of Y in the mafic enclaves (ME) are similar to the RPG.
LREE>HREE is observed in all facies of Huaco granite and associated rocks, with the exception of the garnet-bearing felsic dike (sample 6589). The highest REE contents (>170 ppm) are found in the RPG, BG, APG and ME (Table 1, Fig. 7). The RPG, BG and APG show similar chondrite-normalized REE patterns and La$_n$/Yb$_n$ ratios always >5. The EqG have lower REE contents but similar La$_n$/Yb$_n$ ratios also >5 (Table 1, Fig. 7). The FE, MA and FD have the lowest concentrations of REE and the lowest La$_n$/Yb$_n$ ratios, mostly <5 (Table 1, Fig. 7). The Eu/Eu* ratio is <1 and the La$_n$/Yb$_n$ ratio is >1 for all rocks, with the exception of the FD garnet-bearing sample (Table 1 and Fig. 7).

5. Discussion

Based on Nd and Sr isotopic data (εNd -2.10 to -4.27; Sr$^{87}$/Sr$^{86}$ 0.7820 to 0.8825) and geochemical features such as high and restricted SiO$_2$ contents, peraluminous character, high contents of LIL and other trace elements such Nb, Y and Ga, Grosse et al. (2009) and Dahlquist et al. (2010) suggested that the Huaco pluton, as a whole, formed from a mainly crustal source (possibly the Ordovician meta-granites), with minor participation of a mantle-derived component, and intruded in a dominantly extensional setting. The study of each minor facies and associated igneous rocks can give further clues on the evolution of the granite pluton.

Both the BG and the APG are coeval with the RPG. The BG possibly formed on the walls of the magmatic chamber, whereas the APG formed around the BeP. A temporal sequence of crystallization in the order BG → RPG → APG is favored by the slight decrease in the biotite/muscovite ratio and by their LIL contents (see below). The finer-grained texture of the BG and APG facies compared to the RPG facies suggests faster growth rates for the BG and APG during slightly lower temperature conditions (e.g., Vernon, 1986).

Figures 8a and b present major and trace element variation diagrams with SiO$_2$ (wt%) as a differentiation index for the facies and associated rocks of granitic composition. Although samples of the RPG, BG and APG are fairly scattered in the diagrams, they show rough trends. These trends are better defined for TiO$_2$, Al$_2$O$_3$, ferromagnesian elements, CaO, Ba and Sr, and weakly marked for Na$_2$O, K$_2$O, Cs, Rb, Ba/Rb and REE. Y shows a sub-horizontal tendency and the Rb/Sr ratio a slightly positive tendency. These trends suggest a fractional crystallization process for the RPG, BG and APG, as previously indicated by Sardi et al. (2010, 2011). The remaining rocks appear to be unrelated to these trends, particularly in the cases of TiO$_2$, the ferromagnesian elements, Ba and Sr.

Large-ion lithophile elements such as Rb, Sr, Ba and Cs and their ratios, as well as the REE, are commonly used as monitors of magmatic differentiation (e.g., Halliday et al., 1991; Morteani et al., 1995; Icenhower and London, 1996; Nabelek and Bartlett, 1998; Nabelek, 1999; Jung et al., 2000; Dahlquist et al., 2007). Therefore, we have applied a fractional crystallization model to investigate the behavior of Rb, Sr, Ba and also the REE during this process in the Huaco granite pluton. The used equation is the well-known Rayleigh fractionation: $C_l/C_o = f^{(D-1)}$ (taken from Rollinson, 1998), where $C_l$ is the weight concentration of a trace element in the magmatic liquid; $C_o$ is the weight concentration in the parental liquid, which we consider it to be the BG facies; $f$ is the fraction of melt remaining; and D is the bulk distribution coefficient of the fractionating assemblage during crystal fractionation. The different values of Kd coefficients were taken from Arth (1976), Rapela and Shaw (1979), Nash and Creer (1985) and Icenhower and London (1996).

According to the obtained values of D (D$_{Sr,Ba}$ >1 and D$_{Rb}$<1; Rollinson, 1998), Sr and Ba are considered “compatible elements” and Rb as “incompatible” element. The evolutionary models were calculated assuming a starting melt with 285.9 ppm Rb, 318.5 ppm Ba and 77.5 ppm Sr, which are the average values of the two BG samples. The average values...
FIG. 8. "Harker" diagrams, with SiO$_2$ (wt%) as indicator of differentiation ("x axis") (Only "granitoid" facies and rocks are considered). Variation line is calibrated by least square regressions considering the main and coeval facies (RPG, BG and APG). a. Major elements; b. Trace elements.
of the BG samples were also used for the REE. The mode of fractionating minerals is also an average value of these samples: 37% quartz, 26% K-feldspar; 29% plagioclase; 5% biotite and 3% muscovite.

Figure 9 shows the hypothetical Rb, Sr and Ba compositions in the calculated liquid according to the Rayleigh fractionation model. Comparison between the theoretical compositions and the samples show a correlation for the BG, RPG and APG, whereas the MA, ME, FE, DD, FD and EqG plot away from the theoretical curves, mostly below them. Therefore, we propose that the coeval RPG, BG and APG facies are related to each other by a fractional crystallization process, whereas the other facies and associated rocks were not involved in this process. The REE compositions also show correlation with the fractional crystallization model for the coeval RPG-BG-APG facies, which furthermore have a notable parallelism in the normalized diagrams (Fig. 10a). Probably due to high contents of REE-fractionated minerals (e.g., biotite), the ME plot close to the theoretical model, but we cannot suggest any relation with the main facies by means of this process, at least given the geochemical data (Fig. 10b). The other facies and associated rocks seem to have no relationship with the fractional crystallization model (Fig. 10a, b, and c).

Given their mostly ellipsoidal shapes and the presence of the APG surrounding them, the BeP probably formed when the main RPG was not fully crystallized. Hence, the BeP can be considered coeval to the final stage of the RPG, rather than an independent event. This also applies to the OG (Grosse et al., 2010). The internal structure of the BeP indicates a progressive sequence of crystallization from the aplitic margins (the MA) towards the interior of the intra-granitic pegmatitic cavity (e.g., Cameron et al., 1949; Černý, 1991; Stilling et al., 1996). The BeP and the OG point to the importance of water and/or volatiles in the late stages of crystallization of the main granite. The formation of the BeP and its main accessory mineral, beryl, require conditions of water-saturation and the presence of volatiles (Jahns and Burnham, 1969; Evensen et al., 1999). The circulation of water during pegmatitic crystallization is also manifested by the Na-metasomatism present in the pegmatite bodies (Sardi et al., 2015).

FIG. 9. Sr-Rb (a) and Ba-Rb (b) diagrams showing measured contents and theoretical concentrations obtained from the crystal fractionation model. Cr.: crystallization; TM: theoretical model.
Likewise, high water content and its exsolution probably was the driving force for the formation of the OG (Grosse et al., 2010).

The presence of monazite and other accessory minerals such as apatite can play an important role in LREE fractionation (e.g., Broska et al., 2000; Dahlquist, 2001). Apparently, the behavior of the HREE could have been controlled by the presence of garnet rather than monazite (Duke et al., 1992), as is clearly observed in one sample of the FD. The MA, FE and FD facies with values of \( \text{La}_n/\text{Yb}_n \) generally less than 6, could have formed at a lower temperature than the main regional facies (RPG). The negative Eu anomaly (\( \text{Eu}/\text{Eu}^* <1 \)) observed in several facies and associated rocks of the Huaco granite pluton can be attributed to the fractionation of feldspars. However, the unique positive Eu anomaly observed in one sample of the FD is attributed to garnet as accessory mineral (Fig. 10c) (e.g., Henderson, 1984).

Features shown by the ME suggest that they are mafic magma globules incorporated into the host
granite, i.e., rounded or oval shapes, cooling edges, fine to very fine grained texture, incorporation of host magma megacrysts and presence of acicular apatite, indicative of fast cooling and mingling (e.g., Michel et al., 2016). In addition, the ME have higher εNd values (-0.55 and 0.61; Grosse et al., 2009) than the host granite (εNd_Huaco Granite (RPG facies) -4.27 to -2.10; Grosse et al., 2009), suggesting a more primitive source. On the other hand, the ME have high initial 87Sr/86Sr ratios (0.8586 and 0.8680, Grosse et al., 2009). This decoupling behavior of Sr and Nd isotopes is common in enclaves of this type (e.g., Holden et al., 1991; Lesher, 1990 and 1994; Pin et al., 1990; Allen, 1991). Hence, the ME may be considered primitive remnants of the mafic component of the pluton.

The FE can be considered “premature” aplites that formed when partially crystallized granitic magma “breaks” along planes allowing the intrusion of aplites, which are then dismembered due to the movement of the magma. Alternatively, the FE could have been part of a first pulse of felsic magma that crystallized at the margins of the magma chamber and was later dismantled and incorporated by the main granitic magmas. Remnants of these felsic margins could be the felsic facies described by Rossi et al. (2005b) at the eastern border of the Huaco granite pluton.

The occurrence of the DD suggests that they may correspond to an independent/unrelated and younger episode, since this type of dioritic dikes, cutting felsic igneous bodies, is common in extensional post-orogenic settings (e.g., Hegner et al., 1998).

The EqG are temporally younger than the main facies as they contain enclaves of the RPG. Grosse (2007) had suggested that the EqG originated from a purely crustal source and therefore are not final melts of the RPG. A purely crustal source is in agreement with the lack of tonalitic enclaves in the EqG and their chemical compositions similar to experimental melts derived from crustal rocks (e.g., the peraluminous orthogneisses of Holtz and Johannes, 1991; Grosse, 2007).

6. Conclusions

The Huaco granite pluton (Velasco Range, northwest Argentina) is composed by one main facies (RPG) and two subordinate facies that are coeval and co-genetic (BG and APG), as well as two coeval-to-late co-genetic facies (BeP and OG). In addition, it is host to temporally previous (ME and FE) and posterior (FD, DD and EqG) associated rocks.

Based on field observations, petrography, LIL and REE compositions, the main and coeval facies formed by fractional crystallization from the main magma in the sequence BG-RPG-APG, from the wall towards the interior of the chamber and finally around the Be-pegmatites.

The other units had distinct magmatic evolutions: i) the ME are partially assimilated remnants of mafic, mantle-derived components; ii) the FE are remnants of premature aplites or of an initial felsic pulse; iii) the BeP, FD and OG are related to abundant contents of water and/or volatiles and formed during the final stage of crystallization of the main granitic facies (BeP and OG) or after it (FD); iv) the EqG intruded the RPG and seem to have a purely crustal source, suggesting a second batch of fusion without a mafic component (with the exception of the La Chinchilla stock, which has features suggesting a more primitive source); and v) the DD are possibly associated to a younger episode of mafic, mantle-derived magmatism related to extension, although geochmical data is needed to better constrain its origin.

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