U-Pb ages and Hf isotope compositions of zircons in plutonic rocks from the central Famatinian arc, Argentina

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Article history:
Received 24 August 2016
Received in revised form 11 April 2017
Accepted 12 April 2017
Available online 15 April 2017

Keywords:
Zircon
Hafnium isotope
Ordovician
Famatinian arc

Abstract

The Famatinian arc formed around the South Iapetus rim during the Ordovician, when oceanic lithosphere subducted beneath the West Gondwana margin. We present combined in situ U–Th–Pb and Lu–Hf isotope analyses for zircon to gain insights into the origin and evolution of Famatinian magmatism. Zircon crystals sampled from four intermediate and silicic plutonic rocks confirm previous observations showing that voluminous magmatism took place during a relatively short pulse between the Early and Middle Ordovician (472–465 Ma). The entire zircon population for the four plutonic rocks yields coherent εHf negative values and spreads over several ranges of initial εHf(t) units (−0.3 to −8.0). The range of εHf units in detrital zircons of Famatinian metasedimentary rocks reflect a prolonged history of the cratonic sources during the Proterozoic to the earliest Phanerozoic. Typical tonalites and granodiorites that contain zircons with evolved Hf isotopic compositions formed upon incorporating (meta)sedimentary materials into calc–alkaline metaluminous magmas. The evolved Hf isotope ratios of zircons in the subduction related plutonic rocks strongly reflect the Hf isotopic character of the metasedimentary contaminant, even though the linked differentiation and growth of the Famatinian arc crust was driven by ascending and evolving mantle magmas. Geochronology and Hf isotope systematics in plutonic zircons allow us understanding the petrogenesis of igneous series and the provenance of magma sources. However, these data could be inadequate for computing model ages and supporting models of crustal evolution.

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1. Introduction

Plate–tectonic processes and the Earth’s paleo–geographic history of the western part of South America developed over the past 2.0 Ga during three major orogenic cycles, these arc: the Amazonian Orogenic System that extended from 2.0 to 0.9 Ga, the Terra Australis Orogen that evolved between 0.9 and 0.25 Ga, and the currently active Andean Orogen (Cordani et al., 1973; De Brito Neves and Cordani, 1991; Cawood, 2005; Ramos, 2008; Bahlburg et al., 2009; among others).

The Ordovician Famatinian arc extending from Colombia to Patagonia represents a subduction–related magmatic belt that evolved along the convergent margin of Gondwana during the time of Terra Australis (Cawood, 2005; Ramos, 2008). The Famatinian arc is the largest arc in the paleo–Pacific realm of the West Gondwana (Rapela et al., 1992; Bahlburg and Hervé, 1997; Ramos, 2008). Plate tectonic evolution during the Paleozoic led to fragmentation of the Famatinian arc into distinct segments. In the study region, the arc was shut off due to the collision of a Laurentia-derived microcontinent, called either Precodillera or Cuyania (Thomas and Astini, 1996; Ramos, 2004). The collision and related mountain building stage (ca. 460–400 Ma) that shut the Famatinian arc off also uplifted tilted and unroofed the plutonic crust that had built up during the Early and Middle Ordovician (Astiní and Dávila, 2004; Collo et al., 2009; Mulcahy et al., 2014; Cristofolini et al., 2014; Thomas et al., 2015).

Here we present new U–Pb ages and Lu–Hf isotopic data of zircon grains separated from four plutonic rocks and one...
metasedimentary collected at the sierras Valle Fértil and southern Famatina, the best deep crustal exposure of the Famatian arc (Tibaldi et al., 2013; Ducea et al., 2015a). Our new isotopic data are combined with data of Famatian magmatic zircons available from the literature (Chernicoff et al., 2010; Hauser et al., 2011; Dahlquist et al., 2013; Bahlburg et al., 2016) to further investigate the origin of the Famatian arc and the evolution of the paleo–Pacific margin of the West Gondwana. Our discussion focuses on two related questions: 1) why do isotopically evolved zircons crystallized in calc-alkaline metaluminous plutonic rocks? and 2) what is the relevance of Hf isotope zircon evidence to crustal evolution in the Famatian magmatic arc?

2. Geological setting

2.1. The Famatian arc

Here we briefly present the geological construction of the Famatian arc based on selected studies (Rapela et al., 1992; Mannheim and Miller, 1996; Toselli et al., 1996; Pankhurst et al., 1998, 2000; Coira et al., 1999; Lucassen and Franz, 2005; Ducea et al., 2010; Otamendi et al., 2010a; Bellos et al., 2015; and references therein). The Famatian arc is a well-defined magmatic belt of latest Cambrian to Middle Ordovician plutonic and volcanic rocks extending meridionally for more than 2500 km from Colombia to Patagonia. Along Argentina, this Ordovician arc is exposed from the international border with Bolivia through the Puna and Sierras Pampeanas to the northern Patagonia (Fig. 1). Geophysical data and small outcrops show that the Famatian arc extends all across the Pampa plains where it is the crystalline basement of sedimentary basins (Chernicoff et al., 2010).

The Sierras Pampeanas segment (28° to 33° S) of the Famatian arc exposes plutonic regional–scale Cordilleran–type batholiths (Fig. 1). The Famatian batholith includes an I-type dominated plutonic belt extending along side to a S-type dominated belt (Toselli et al., 1996; Pankhurst et al., 2000; Rossi et al., 2002). Within the Sierras del Famatina, Los Llanos, Chepes, Ulapes, La Huerta and Valle Fértil, the most abundant igneous rocks making up regional–scale batholiths are calc–alkaline metaluminous I–type granitoids, whereas weakly or strongly peraluminous felsic granitoids are less abundant but still widespread (Toselli et al., 1996; Pankhurst et al., 1998; Sims et al., 1998). The opposite is the case in other ranges dominated by peraluminous and silicic Famatian plutonic rocks, among them sierras de Fiambalá, Capillita, Zapata, and in part sierra de Velasco are the best examples (Toselli et al., 1996; Rossi et al., 2002; Bellos et al., 2015).

Located at the north-western corner of the Sierras Pampeanas, the type locality of the Famatian arc is exposed along the Sierras del Famatina (Acenolaza and Toselli, 1976). The lowest stratigraphic unit within the Sierras del Famatina consists of metasedimentary rocks derived from turbidites deposited during the early and middle Cambrian (Collo et al., 2009). The early Paleozoic volcano-sedimentary successions unconformably overlaid folded low grade metamorphic basement (Acenolaza and Toselli, 1976; Astini, 1998). The Ordovician sedimentary, volcano-sedimentary and volcanic rocks of Famatina exceed 3000 m thick (Mangano and Buatois, 1996; Astini, 1998). Ordovician stratigraphic sequences include siliciclastic and carbonaceous sediments deposited predating Famatian magmatism and volcano-sedimentary deposits inter-stratified with lava flows or intruded by plutonic bodies (Mangano and Buatois, 1996; Astini, 1998; Cisterna and Coira, 2014). Volcanic rocks have variable compositions ranging from basalt to rhyolite. The most common lava types are basalt and rhyolites, but a range of different compositions between basalt and rhyolite occurs in the volcaniclastic successions (Mangano and Miller, 1996).

Subduction–related magmatic activity in the central section of the arc (in Argentina) ended at about 465 Ma when an allochthonous terrane collided against the Gondwana margin (Thomas and Astini, 1996; Astini and Dávila, 2004; Ducea et al., 2010, 2017). The collisional event fragmented the Famatian arc into two segments with contrasting stratigraphic features and syn-collisional geologic evolutions. For this reason, between 21° and 27° S in the Puna plateau, the early Ordovician magmatic arc is now at the Argentinean-Chilean border on the Puna (Bahlburg et al., 2016), and hence it is westward located with respect to the time-equivalent plutonic belts on the Famatina and the Sierras Pampeanas (Pankhurst et al., 1998; Ducea et al., 2010). In contrast, within the Puna plateau the main phase of Famatian plutonism occurred during the Upper Ordovician (ca. 444 Ma) and is exposed over 400 Km along the Faja Eruptiva de la Puna Oriental (Coira et al., 1999, 2009; Kleine et al., 2004; Bahlburg et al., 2016).

The present–day architecture of various exposed fragments of the ancient Famatian arc is influenced by structures formed by Gondwanides and modern Andean tectonics. However, major geological features such as the absence of Ordovician volcano-sedimentary successions to the south of the Sierras del Famatina and a sharp increase of the exposed paleo-depths at about the same latitudes are Paleozoic (Cristofolini et al., 2014). If the lower crustal rocks exposed in the Sierras Pampeanas are the equivalents of volcanic and plutonic rocks in the western Puna, the Famatian arc crust exposes a window of about 30 km structural thickness, in which the majority of rocks are magmatic and related to the Cambro–Ordovician subduction zone magmatism. A striking feature of the Famatian arc is the general lack of older basement within the exposed arc crustal section; instead the only country rocks to the Famatian arc (even when exposed at deep crustal levels) are metasedimentary assemblages. Older zircons are only found in orthogneisses from the Antofalla block, in the southern Puna (Escayola et al., 2011), and perhaps that is the only area in which old basement rocks are documented to exist as country rocks. Nevertheless, the metasedimentary successions, which surround the Famatian batholith, contain older detrital zircons, indicating that the regional-scale country host rocks for Famatian magmatism came from the nearby west Gondwana continental margin (Collo et al., 2009; Cristofolini et al., 2012; Bahlburg and Berndt, 2016).

2.2. The Famatian batholith from the eastern Sierra de Valle Fértil and the southern Sierras del Famatina

Plutonic rocks from the eastern Sierra de Valle Fértil and the southern Sierras del Famatina are part of the Famatian batholith (Toselli et al., 1996; Pankhurst et al., 2000). The batholith ranges in composition from rare gabbro through (quartz) diorite, tonalite, granodiorite, and granite (Pankhurst et al., 1998; Otamendi et al., 2010a). Peraluminous leucogranites are generally intermingled with metaluminous plutonic rocks. Most plutonic rocks are hornblende bearing, with biotite and magmatic epidote appearing in tonalites, granodiorites and granites.

Our ongoing geological and petrological studies from eastern Valle Fértil to southern Famatina reveal several plutons, which are grouped into 3 units. Like the Famatian batholith itself, the plutons are aligned north–south and extend over kilometres in length as uplifted by Andean faults. The Valle Fértil transitional silicic unit comprises three plutons and extends northward from the centre of the Sierra de Valle Fértil to the town of Usno (Fig. 2). The three plutons have gradational and complex contacts, and they could alternatively be interpreted as internal variations of igneous magmas within an elongate plutonic body. The plutons are distinguished by the relative abundance of
diörites, tonalites and leucogranites, but all of the plutons show intermediate rocks commingled with leucogranites. In the eastern (i.e. upper) parts of the transitional intermediate unit, tonalites display an increase in the modal abundance of quartz and biotite, and include lens-shaped bodies of granodiorites.

The Valle Fértil silicic unit comprises three plutons. From south to north these are: Las Tumanas pluton largely characterized by coarse-grained inequigranular granodiorites; Quimilo pluton monotonically formed by porphyritic granodiorites with K-feldspar megacrysts; and San Agustín pluton dominated by equigranular...
biotite and hornblende granodiorites intimately intermingled with tonalitic and leucogranitic veins. The three plutons contain inclusions of amphibole gabbroic rocks and granulitefacies metasedimentary rocks. Blocks of amphibole-rich gabbroic rocks are frequent among plutonic tonalites and granodiorites. Metasedimentary country rocks are included as tens of meter long blocks scattered throughout the plutonic rocks. Primary foliation in the granodiorites and tonalites is defined by flattened mafic inclusions and planar orientation of plagioclase, hornblende and biotite crystals. Inclusion swarms occur at almost all locations and are generally concordant with a subvertical primary foliation (Castro et al., 2008).

The Cerro Blanco silicic unit is the northern extension of its equivalent at Valle Fértel. The boundary between the two silicic units is to the north of Usno, but of unresolved nature because of the Quaternary covers (Fig. 2). The Cerro Blanco silicic unit differs in having distinct lithologic constitution and higher emplacement levels than the Valle Fértel silicic unit. The Cerro Blanco unit consists
of a northern zone of biotite hornblende tonalites through subordinate granodiorites and a southern zone of biotite granite with quartz–rich tonalite. The metasedimentary rocks scarcely occur as meter-scale angular blocks and show greenschist-facies mineral assemblages, suggesting upper crystallization paleo-depths comparable to the silicic unit at the Sierra de Valle Fértil. The gabbroic inclusions are in all the scales from small lens-shaped enclaves to km-long bodies.

Toward the north of the Cerro Blanco area, sharp topographic differences at the present erosion level show that the Famatinian batholith built up into the Cambrian Negro Peinado Formation and generated flat rooted plutons forming the crest of the Famatina mountain ranges (Collo et al., 2009). In fact, most of the highest topographic elevations are of the Cambrian country rocks, not the Ordovician granitoids.

Along the western margin of Valle Fértil, the Famatinian intermediate-batholith gradually changes composition toward the Valle Fértil mafic complex, a large mafic–ultramafic section of middle and lower Ordovician crust (Otamendi et al., 2009, 2010; Walker et al., 2015). The Valle Fértil mafic complex is dominated by gabbro-norite and diorite associated with lens-shaped bodies (at least 10 km wide) of mafic and ultramafic cumulate sequences (peridotites, dunite, troctolite, olivine gabbro-norites and amphibole gabbronorite). The geological contexts allow us observing a complete arc middle crustal section of the Famatinian batholith bracketed from the bottom and the top (Tibaldi et al., 2013).

Within the Sierra de Valle Fértil, Pankhurst et al. (2000), Ducea et al. (2010) and Castro et al. (2014) report more than a dozen U–Pb zircon crystallization ages ranging from 476 to 469 Ma for tonalites and granodiorites that constitute the batholith (Fig. 2a).

2.3. Petrographic and geochemical features of the plutonic rocks

Four samples of Famatinian plutonic rocks were collected for U–Pb zircon dating. All of the four specimens are intermediate to silicic plutonic rocks (Table 1) and their geographic distribution spreads over a large region of the Famatinian batholith (Fig. 2b).

Granodiorites (samples GUS3 and PG2) and tonalite (sample GCB1) represent the most common plutonic lithologies in the silicic units. Quartz and plagioclase are the dominant felsic phases in most plutonic rocks; microcline occurs as irregular lath-shaped grains with inequigranular texture or as subhedral tabular megacrystals in porphyritic granodiorite. Tonalites and granodiorites have green prismatic amphibole and pale red–brown biotite; they commonly contain epidote, apatite, sphene, oxide, allanite and zircon as accessory phases. Although the great majority of the rocks show pristine igneous structures, the existence of post-magmatic deformation is strong in Pagano granodiorite (sample PG2) and incipient in the tonalite from Cerro Blanco (sample GCB1). Mineral foliation is associated with deformation and re-crystallization of minerals as reflected by strained extinction of quartz and feldspars, curved laths of biotite, and development of polycrystalline aggregates with ribbon texture. Sample GVF58 is representative of granite (GUS3) and all three are magnesian (not shown).

The majority of the intermediate and silicic plutonic rocks have a Zr concentration ranging from 130 to 220 ppm. The Zr solubility predicted that melts with the composition of the studied rocks reach Zr saturation at temperatures between 800 and 850 °C (Fig. 3b). Rocks present contrasting rare earth elements abundances shown in chondrite-normalized (REEN) patterns (Fig. 3c). According to the Frost et al. (2001) classification scheme, two plutonic rocks (GVF58 and GCB1) are calcic and the third (GUS3) is calc-alkalic, and all three are magnesian (not shown).

The majority of the intermediate and silicic plutonic rocks have a Zr concentration between 130 and 220 ppm. The Zr solubility models of Watson and Harrison (1983) and Boehnke et al. (2013) predict that melts with the composition of the studied rocks reach Zr saturation at temperatures between 800 and 850 °C (Fig. 3b). Rocks present contrasting rare earth elements abundances shown in chondrite-normalized (REEN) patterns (Fig. 3c). TheREE pattern of granite (GVF58) is strongly fractionated with LREE/YB of 30, and shows an anomaly of the Eu—anomaly. Granodiorite (GUS3) has low zREE, moderately fractionated REE patterns (LREE/YB = 5.4) and a slightly positive Eu anomaly. This granodiorite also seems to have a weak concave upward pattern from MREE to HREE. Tonalite (GCB1) exhibits the highest zREE contents among the rocks chosen to study zircons, with a REE pattern characterized by concentrations that are depleted in LREE and enriched in HREE.
minor fractionation and a marked negative Eu anomaly.

3. Methodology and data treatment

Zircon U–Pb geochronology was performed by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) at the Arizona Laserchron Center, University of Arizona. All the analysis followed protocols described in detail by Gehrels et al. (2008). Minor adaptations to the general protocols are described in Ducea et al. (2010). Zircon U–Pb age results were plotted in conventional concordia diagrams associated with stacked histograms using the Isoplot 3.0 Excel macro of Ludwig (2003). In order to investigate core–rim age relationships we analyzed two spots in large euhedral zircons. All of the measured dataset are plotted on the U–Pb conventional concordia diagrams that exhibit zircons with inherited ages. A subset of U–Pb age results that were chosen for computing the weighted mean age are shown separately in best age plots.

In this study we report zircon Hf isotope geochemistry of four plutonic rocks and one metasedimentary rock. In situ Hf isotope measurements were performed on the same four plutonic rocks (8–10 grains analyzed from each sample) as used to obtain U–Pb zircon ages. Hf isotope measurements were also conducted on 20 detrital zircons in sample VFNO49 studied by Cristofolini et al. (2012). Zircon Hf isotope geochemistry was measured by laser ablation at the Arizona Laserchron Center on a Nu multicollector ICP–MS instrument. The instrumental characteristics, the accuracy and reproducibility of Hf isotopic measurements as compared to Hf solution analysis, and the followed protocols have been discussed in detail by Cecil et al. (2011).

Because the U–Th–Pb and Hf isotopic data were acquired at different times using the same mounts of previously dated zircons, and hence further drilling the same spots, a potential situation is that the pits drilled for U–Pb and Hf measurement are sampling different zircon growth zones (Cecil et al., 2011). In the particular case of igneous rocks, this problem is less critical because most zircons are large crystal and show broad zoning without discernible inherited cores. Although, detrital zircons are small and exhibit intricate zoning, the age used to calculate the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of detrital zircons is that measured through U–Pb dating in each grain. Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are reported as $\epsilon_{\text{Hf}}$, which represents the isotopic composition at the time of crystallization relative to the chondritic uniform reservoir. In this study Hf isotope compositions are expressed as deviations (in parts per 10^4) from that of CHUR, whose Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ values are assumed to represent those of the Bulk Silicate Earth. The $\epsilon_{\text{Hf}}$ values were calculated using the $^{176}\text{Lu}$ decay constant of Scherer et al. (2001) and the chondrite values of Bouvier et al. (2008). Depleted mantle Hf model ages were approximated to the time of crystallization using the present—day depleted mantle isotope composition of Vervoort and Blichert-Toft (1999).

The total isotopic datasets for U–Pb and Hf analyses are available in Supplementary data tables A1, A2 and A3 and summarized in Table 2.

4. Results

4.1. U–Pb geochronology

Four samples were analyzed for U–Pb geochronology with an average of about twenty zircons from each sample. The four

![Fig. 3. (a) Harker-type diagram showing whole rock variation of ASI index ($\text{ASI} = \text{Al}_2\text{O}_3/\text{(CaO + Na}_2\text{O + K}_2\text{O}$ on a molar basis) against SiO$_2$. Studied plutonic rocks are projected with representative variation for plutonic rocks from the Sierras de Valle Fertil and La Huerta taken after Otamendi et al. (2012). (b) Projection of whole rock abundances of Zr against SiO$_2$ using same data as in panel (a). Lines mark the limit of the zircon saturated field in the Zr vs. SiO$_2$ space. Zircon saturation was estimated using models calibrated by Watson and Harrison (1983) and Boehnke et al. (2013) and assuming a melt with an ASI = 1. (c) REE whole-rock patterns normalized to C1 chondrite.](image-url)
plutonic rocks contain homogeneous populations of zircon grains in terms of shape, size and colour. Zircons were studied with SEM in backscatter electron mode and cathodoluminescence (CL). Backscatter electron and CL images show that compositional zoning is similar among all of the specimens. The zircons are typically prismatic, euhedral to subhedral, clear, transparent and vary in size from 50 to 400 μm. The majority of the zircons show internal oscillatory zoning and rare inherited components or growth rims.

In granite GVF58, zircon morphology is simple, with prismatic, isometric and roundly zoned as the prevalent type. Most zircons also show simple CL patterns from a bright dominant interior to slightly dark outer zones. Fifteen spots were analyzed in ten zircon grains. Middle zones with typical early Ordovician ages have high U contents of up to 1644 ppm, and a large majority of the zircons have Th/U ratios >0.3 with most Th/U values ranging from 0.5 to 0.9. The best age determination for this sample is estimated from a coherent cluster of six points with a weighted mean 206Pb/238U age of 471.5 ± 4.4 Ma (Fig. 4a–c). Only an inherited core yields a concordant age at 503 Ma (Fig. 4a–c).

Tonalite GUS3 was collected in a fault-bounded plutonic block located 15 km to the north of the town of Usno and sampled the centre of the Cerro Blanco unit (Fig. 2b). Twenty three spot measurements were made in the tonalite (GUS3) including three core rim pairs and two of single cores. Twenty measured U/Th ratios fall in a narrow range of between 0.3 and 0.6. Three spots that have U/Th < 0.24 and U < 326 ppm were rejected because yield high error (>15%) and deviation, and discordant ages (>10% of discordance). The population of zircon ages records the inheritance commonly found in Famatinian plutonic rocks (Ducea et al., 2010). One core yields Grenvillian age of 1103 ± 19 Ma (100% concordant) and another yields Brazilian orogenic age of about 618 Ma (Cordani et al., 1973). The Ordovician age is extracted from seven data that give concordance with a weighted mean 206Pb/238U ages of 467.8 ± 3.1 Ma (206Pb/238U age at 471.5 ± 4.4 Ma (Fig. 4a–c). Only an inherited core yields a concordant age at 503 Ma (Fig. 4a–c).

Granodiorite GCB1 was collected from the Cerro Blanco pluton at the southern tip of the Sierras de Famatina (Fig. 2b). Nineteen out of twenty one analyzed spots yield 206Pb/238U ages that are within the range between 479 and 464 Ma (Fig. 5a–b). One zircon yields a Middle Cambrian best ages of 518 Ma (94% concordance) reflecting core inheritance from metasedimentary host successions (e.g. Collo et al., 2009; Cristofolini et al., 2012). Another 206Pb/238U age of 500 Ma may imply some zircons have rejuvenated inheritance from either Cambrian or older ages. The best-constrained age is revealed by seven data that give concordance with a weighted mean on 206Pb/238U ages of 470.7 ± 4.3 Ma with an MSWD <1 (Fig. 5b). Moreover, the best age closely correspond to the peak of the Gaussian distribution (Fig. 5c).

Sierra de Paganzo granodiorite (PG2) was taken 45 km to the east of Cerro Blanco granodiorite at another southern tip of the Sierras de Famatina (Fig. 2b). Twenty three measurements were obtained in eighteen zircons from specimen PG2. Only one grain has an inherited core of Neoproterozoic age (622 Ma) corresponding to the Brazilian orogenic cycle. The remaining 22 spot analyses yield 206Pb/238U ages ranging from 490 to 451 Ma (Fig. 5d). All of these zircons have Th/U ratios between 0.4 and 1.1, exhibit subhedral or euhedral crystal morphology and well develop internal zoning. Therefore, a somewhat arbitrary standard statistical criterion was used to evaluate the best age. Five spot measurements with nearly perfect overlapping of 206Pb/238U ages were extracted from the 22 data set. The weighted average of the 5 analyses on 206Pb/238U ages is 467.8 ± 3.1 Ma with an MSWD = 0.18 (Fig. 5e).

Significantly, the best extracted age exactly falls in the maximum peak of the Gaussian curve to the age spectra (Fig. 5f).

### 4.2. Lu–Hf isotopes

About eight zircons dated through U-Pb geochronology were selected for Hf isotopes in each plutonic sample. The majority of the chosen zircon grains have ages within the range of active magmatic stage of the Famatinian arc.

Table 2 summarizes the Hf isotope data obtained from zircons of the four plutonic rocks. The magmatic zircons from the four igneous plutonic rocks have similar 207Hf/206Hf ratios (0.0006–0.0023) and 207/206Hf (0.282722–0.282486) with initial εHf(0) values essentially negative (−0.4 to −8.7). Hf model ages calculated relating the initial 207Hf/206Hf composition of zircons to the Depleted Mantle (DM) isotopic composition are calculated assuming a typical 207Hf/206Hf value of 0.1115 for the felsic continental crust. Most igneous zircons have initial high DM model ages clustering at about 1525 Ga but the population of zircons spans the range from 1.3 to 1.7 Ga. A few inherited grains have εHf(0) (500 Ma) values of −0.9, −2.3 and −5.6 that also fall within the same range as magmatic zircons. Although the spread εHf(0) values broadly overlap within error, the Paganzoh granodiorite (PG2) extend to higher εHf(0) and have in terms of εHf(0) the largest amount of little evolved zircons. By contrast, the Cerro Blanco tonalite (GCB1) contain the most evolved magmatic zircons which have εHf(0) lower than −3.7 (Fig. 6d).

The U–Pb ages of the zircons selected for Hf isotope analyses range from 490 to 2195 Ma with most grains falling between 503 and 540 Ma (e.g. Cristofolini et al., 2012). Except for three grains, all of the zircons yield 176Lu/177Hf ratios between 0.0002 and 0.0020 (Fig. 7a). Present–day 176Hf/177Hf ratios are within the range from 0.282272 to 0.282486, corresponding to present–day εHf between −10 and −55. The initial εHf(0) value at the time of zircon crystallization ranges from −7.7 to +2.8 (Fig. 7b). Grains with positive εHf(0) make about a quarter of the detrital zircon population and reflect the subordinate presence of a juvenile component. A graphical appreciation of the Hf isotope composition suggests that the dominant population of detrital zircons project back to a Paleoproterozoic formation age. Since the greywacke-derived metasedimentary rocks (VFNO49) has a maximum depositional age of the middle Cambrian Negro Peinado Formation and its oldest prevailing protolith is Paleoproterozoic, a time span of about 1.5 Ga of zircon (re)crystallization is potentially retained in these detrital zircons (also see Collo et al., 2009).

### 5. Discussion

#### 5.1. Geochronology of the central Famatinian batholith

U-Pb ages of the Famatinian plutonic rocks exposed in the area investigated here fall in the 472 to 465 Ma range, corresponding to a high flux magmatic episode over the lifetime of the central Famatinian arc (Ducea et al., 2017). Excluding discordant and inherited ages, the spread in individual ages for each sample is within

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**Table 2**

Summaries of U-Pb and Hf isotope zircon data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U-Pb</th>
<th>Th/U</th>
<th>U (ppm)</th>
<th>Hf εHf (initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GVF58</td>
<td>471.5 ± 4.4</td>
<td>0.18–0.94</td>
<td>233–1664</td>
<td>(−) 0.89–8.72</td>
</tr>
<tr>
<td>GUS3</td>
<td>464.6 ± 4.1</td>
<td>0.11–0.61</td>
<td>69–1387</td>
<td>(−) 2.13–8.36</td>
</tr>
<tr>
<td>GCB1</td>
<td>470.7 ± 4.4</td>
<td>0.64–1.16</td>
<td>126–511</td>
<td>(−) 3.70–5.86</td>
</tr>
<tr>
<td>PG2</td>
<td>467.8 ± 3.1</td>
<td>0.48–1.29</td>
<td>255–1064</td>
<td>(−) 0.40–5.29</td>
</tr>
</tbody>
</table>

The total U-Th-Pb measurements and Hf isotope composition is available in the [electronic supplementary data tables A1, A2 and A3.](#)
analytical error, and are therefore interpreted to represent statistical dispersion of a single age (Fig. 8). These ages are taken to reflect the time span of crystallization of the Famatinian batholith from the Sierra de Valle Fertil to the southern Sierras del Famatina, and the overall results are consistent with the range of ages reported by previous geochronological results (Pankhurst et al., 2000; Ducea et al., 2010, 2017; Casquet et al., 2012; Dahlquist et al., 2013; Castro et al., 2014).

5.2. Isotopic evolution of Hf during bulk assimilation of metasedimentary rocks into mafic melts

Hybridization between mafic melts originating from the mantle wedge in subduction systems and continental crustal materials is often regarded as a process which broadly amount to two-component mixing (Faure, 1986; Gray, 1984; Beard, 2008). Below we present a model that simulates bulk assimilation of highly-
melted metasedimentary (supra)crustal rocks into mantle-derived mafic melts to assess the extent to which a petrologic mixture can reflect the isotopic data in this oversimplified two end-member process.

The concentration of a chemical component in a mixing line is simply calculated using regular modelling (Faure, 1986). The mixing equation for two components with isotopically distinct Hf is:

\[
\frac{^{176}Hf}{^{177}Hf}_{mix} = \frac{Hf_{M}^{^{176}Hf} \left( \frac{^{176}Hf_{M}}{^{177}Hf_{M}} - \frac{^{176}Hf_{C}}{^{177}Hf_{C}} \right)}{Hf_{mix}^{^{176}Hf} \left( Hf_{M} - Hf_{C} \right)} + \frac{Hf_{M}^{^{176}Hf} - Hf_{C}^{^{176}Hf}}{Hf_{M} - Hf_{C}}
\]

where \(Hf_{mix} = Hf_{M}f + Hf_{C}(1-f)\) with \(f = \frac{X_M}{X_M + X_C}\) and \(X\) is the weights of the two components in a given mixture, wherein letters

Fig. 5. (a and d) Conventional concordia diagrams for zircons from samples GCB1 and PG2, respectively. Errors are shown as ellipses at the 2σ level. (b and e) Bars plot displaying spot used to calculate the weighted mean age for samples GCB1 and PG2, respectively. (c and f) Combined histograms overlain by true probability plots, illustrating the zircon age spectrum for samples GCB1 and PG2, respectively. The number of analyses (y-axis) gives the number of ages which fall in each histogram bin. Ages are taken from \(^{206}Pb/^{238}U\) analyses.
M and C stand for mantle and crust, respectively.

Because most Hf budget of igneous rocks resides in zircons, the behaviour of zircon drives the distribution of Hf in a melt — minerals magmatic system (Watson and Harrison, 1983). Bulk assimilation involves the entire mineral assemblage dissolved from the solid assimilant (metasedimentary rocks) and crystallized from an assimilating mafic melt; however, the rate between dissolution and crystallization of zircon controls the amount of Hf in the melt (Watson, 1996; Bindeman and Melnik, 2016). Thereby, the procedure for modelling mixtures of melts and crystals as developed by Beard 2008 can be reduced to one in which the weight fraction of zirconium available during mixing determines the bulk abundance of Hf and influences on the Hf isotope composition of zircon in the mixture. It is not simple to develop quantitative models to constraints all the variables involved in the evolution of Hf isotopes during mixture of magmas and crustal rocks, and no such model provides unique answer given its multiple unknowns (Farina et al., 2014) With those limitations in mind, we construct a model based on measurable data that explains the composition of Hf isotope composition of plutonic zircons and that is at the same time consistent with field observations and petrological constraints.

Current understanding shows that the Famatinian batholiths grew up into thick mostly marine sedimentary sequences.
deposited in basins onto and outboard of land-masses from the western Gondwana. Our approach uses the available zircon Hf isotope data for two very low grade metasedimentary rocks from northwestern Argentina (BNM207 and BRB163 taken after Hauser et al., 2011) and the metasedimentary rock from the Valle Fertil section from this study (VFNO49). The age distribution and Hf isotope composition of the chosen crustal end members is similar to those of other metasedimentary rocks deposited onto middle and upper Paleozoic basins along the western Gondwana margin (Bahlburg et al., 2009; Reimann et al., 2010; Bahlburg and Berndt, 2016). Furthermore, as Fig. 9a illustrates inherited zircons in plutonic rocks from the eastern Faja Eruptiva within the Puna also have similar ages and isotope composition (Bahlburg et al., 2016).

The mantle-derived highly-melted end member is assumed to have a Hf initial isotope ratios between five and ten times higher than the early Ordovician (470 Ma) CHUR, with the same Hf absolute contents as the primitive melts from the Sierra de Valle Fertil rocks (Fig. 9b). The mantle component is constrained through data from the most primitive Famatinian mafic rocks that left behind sources with Nd initial isotope ratios close above to that of the coexisting CHUR (Casquet et al., 2012; Otamendi et al., 2012; Walker et al., 2015). The Hf isotope composition of all of the end members and those of the igneous zircons from Early Ordovician Famatinian plutonic rocks are shown in Fig. 9b.

In the simplest model, detrital zircon existing in the metasedimentary assimilant is completely dissolved into the assimilating mafic melts. When the magmatic system cools and the melt fraction decreases, the crystallizing melt reaches the zircon saturation point, and hence zirconium (and hafnium) dissolved in the melt is massively incorporated into the crystallizing zircons, which will crystallize in isotopic equilibrium with the melt (Belousova et al., 2006). It follows that the amount of Hf released by the solid assimilant is equal to the weight fraction of zircon in a given metasedimentary rock multiplied by the average concentration of Hf in zircons bulk assimilation of metasedimentary rocks into the magmatic system results in an input of Hf between 3.3 and 7.7 ppm that is from two to six times higher than the Hf concentration in an arc primitive magma (Fig. 9b and c).

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models, and have similar Hf isotopic compositions ($\epsilon_{\text{Hf}}(470) = -4.55 \pm 0.30$) but distinct Hf absolute contents. This simply can reflect distinct fraction of zircon in the original assimilated crustal component (Fig. 9d).

The modelled mixing lines are successful in accounting for the relative variation of bulk Hf contents and isotopic Hf ratios of the plutonic zircons. The model results best satisfy the chemistry of zircons from the plutonic rocks when the mixing tests use a fraction of the crustal end-member slightly lower than 50%. The models, however, cannot reproduce the full range of $^{176}$Hf/$^{177}$Hf versus Hf data for tonalites, granodiorites and granites. The difference is, in part, due to the fact that zircon from some plutonic rocks span over an ample range that lies outside $^{176}$Hf/$^{177}$Hf versus Hf compositional variations of the crustal end members (Fig. 9d).

5.3. Implications of Hf isotopes in zircon for the interpretation of Famatinian magmatism

$\epsilon_{\text{Hf}}(470)$ of zircons from the Early Ordovician plutonic rocks of the Valle Fértil and southern Famatina area are isotopically evolved ($\epsilon_{\text{Hf}}(470)$ values fall below the chondritic uniform reservoir, or CHUR), which is consistent with previous measurements by Chernicoff et al. (2010) and Dahlquist et al. (2013) from elsewhere in the Famatinian arc (Fig. 9d).

Famatinian granodiorites and tonalites bearing zircons with evolved Hf isotopic signatures are magnesian, calcic, and range from metaluminous to weakly peraluminous. This Hf isotopic chemistry of zircons is not what one would expect from a typical intermediate calc-alkaline plutonic rock (Belousova et al., 2006;
Villaros et al., 2012). Here the difference between predicted and observed can be the Hf isotope composition of zircon reflecting the mixture of a reservoir derived from the mantle with the local supracrustal component representing the high grade country rocks exposed in Valle Fértil (Fig. 9).

Several processes converge to produce isotopically evolved zircons in rocks with bulk chemistry still reflecting a typical calc-alkaline igneous magma, among which the main are: 1) subalkaline intermediate plutonic rocks are hybrids of two end members one of which is supracrustal sediments (Kemp et al., 2006); 2) the Hf isotope signature of the hybrid rocks is largely driven by pre-existing crystalline zircons released from the sedimentary contaminants and dissolved into evolving magmas (Kemp et al., 2007); and 3) a dominant population of pre-existing zircons in the crustal materials had isotopically evolved Hf compositions before being incorporated into evolving igneous magmas (Bahlburg et al., 2009, 2016; Reimann et al., 2010; Hauser et al., 2011; this study).

The existence of inherited zircons in the plutonic rocks of the Famatinian batholith and the eastern Faja Eruptiva reflect the presence of pre-existing crust, even when the amount of inherited grains is subordinated to magmatic zircons (Ducea et al., 2010; Bahlburg and Berndt, 2016). By using zircon saturation models we estimate that almost all inherited zircons dissolve into the Famatinian intermediate and silicic magmas (Fig. 3b). Dissolution and precipitation of zircons in an igneous system typically takes place over a few ten thousand years (Watson, 1996; Bindeman and Melnik, 2016) a time span that is much shorter than life-time of an arc volcano and its plumbing system (Claiborne et al., 2010; Ducea et al., 2015b). Since, sedimentary-derived zircons are mostly dissolved into high temperature magmas as those from the Famatinian arc, the hafnium isotopic signature of detrital zircons from regional scale host rocks provide evidence on explaining why characteristically calc-alkaline plutonic rocks bear isotopically evolved Hf evolved zircons. Detrital zircons of the metasedimentary rock (VFNO49) from the northern Sierra de Valle Fértil include a significant evolved component, because about 80% of the zircons have negative εHf(t). Furthermore, this metasedimentary rock has prevailing Pampean 505–540 Ma and Grenvillian 950–1290 Ma sources corresponding to 40% and 25%, respectively, and both sources provided an input of evolved zircons (Figs. 6 and 9a). Nevertheless, it is the incorporation of metasedimentary materials into intermediate and silicic magmas that explain the Hf composition of magmatic zircons in the Ordovician plutonic rocks.

The implication for using zircon isotopic composition to work out the geodynamic setting and crustal evolution here or elsewhere in intermediate rocks is that the incorporation of un–radiogenic Hf from the metasedimentary contaminant plays a major role in the average Hf isotope ratios of the magmatic zircons in the plutonic rocks. Negative isotopic Hf ratios of plutonic zircons are generally interpreted to reflect crustal reworking with lesser to nonexistent production of new continental crust derived primary from mantle sources. The lack of δ18O isotopic data in zircon from our study makes it impossible to discern magmatic zircons crystallized within pure juvenile melts from those that formed within mixed magmas which have one component formed by supracrustal reworking (Valley, 2003; Kemp et al., 2006, 2007). Magmatic zircons within a mixture of mantle magmas and metasedimentary rocks have Hf isotopes composition evolved towards crustal-like component (Fig. 9). Hybridization thereby affects the interpretation of model ages and their implications for model of crustal evolution (Arndt and Goldstein, 1987). From the perspective of Hf isotope compositions, the calc-alkaline Famatinian plutonic rocks can be products of similar mixing proportions between a mantle-derived igneous end member and a sedimentary-derived crustal component. Therefore, the Hf isotope composition of these plutonic zircons cannot be utilized exactly to support models of crustal evolution. Rather, Hf in zircons is useful for observing provenance and constraining petrogenetic models.

6. Conclusion

The central segment of the Famatinian batholith exposed in the Sierra de Valle Fértil and the southern Sierras del Famatina was formed over less than 10 Ma. Almost all of the plutonic rocks making up this segment of the batholith crystallized between 475 and 465 Ma. Mineralogy and geochemistry of intermediate and silicic plutonic rocks is typical and characteristic of subduction–related igneous rocks. The evolved character of the Hf isotopic composition of magmatic zircons is modelled to be caused by the incorporation of a metasedimentary component incorporated into evolving mantle-derived and crustally differentiating calc–alkaline magmas. The Famatinian plutonic rocks have zircon Hf isotope composition and whole rock radiogenic isotope signature that obscure observing their lineage (also see Ducea et al., 2015a). The presence of evolved Hf plutonic zircons within calc–alkaline intermediate plutonic rocks cannot be used to assert whether the Early Paleozoic Gondwana margin evolved through pure crustal recycling or involved net growth of continental crust.

Acknowledgments

We acknowledge thorough and constructive reviews by Maximiliano Naipauer and an anonymous reviewer, whose comments and criticism have significantly improved the quality of the manuscript, as well as guidance from journal regional editor Víctor Ramos. This work was funded by ANPCYT-Argentina through grants PICT 0453/10 and 0958/14, and SeCyT-UNRC grant PIP2012/18/C423. We acknowledge support from Romanian Executive Agency for Higher Education, Research, Development and Innovation Funding project PN-II-ID-PCE-2011-3-0217 to MND. Argentinean researchers are supported by Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jsames.2017.04.005.

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