REVIEW ARTICLE

Andalusite and Na- and Li-rich cordierite in the La Costa pluton, Sierras Pampeanas, Argentina: textural and chemical evidence for a magmatic origin

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Abstract The La Costa pluton in the Sierra de Velasco (NW Argentina) consists of S-type granitoids that can be grouped into three igneous facies: the alkali-rich Santa Cruz facies (SCF, SiO₂ ~67 wt%) distinguished by the presence of andalusite and Na- and Li-rich cordierite $(Na_2O = 1.55 - 1.77 \text{ wt\%} \text{ and } Li_2O = 0.14 - 0.66 \text{ wt\%}), \text{ the}$ Anillaco facies (SiO₂ \sim 74 wt%) with a significant proportion of Mn-rich garnet, and the Anjullón facies (SiO₂) \sim 75 wt%) with abundant albitic plagioclase. The petrography, mineral chemistry and whole-rock geochemistry of the SCF are compatible with magmatic crystallization of Na- and Li-rich cordierite, and alusite and muscovite from the peraluminous magma under moderate P-T conditions (\sim 1.9 kbar and ca. 735°C). The high Li content of cordierite in the SCF is unusual for granitic rocks of intermediate composition.

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J. Saavedra CSIC, Instituto de Agrobiología y Recursos Naturales, 37071 Salamanca, Spain **Keywords** Andalusite · Na- and Li-rich cordierite · S-type granite · La Costa pluton · Sierras Pampeanas

Introduction

Andalusite and cordierite are important and common rockforming minerals in metapelitic rocks and may also be abundant in felsic peraluminous igneous rocks such as granites, pegmatites, aplites and rhyolites. A fundamental question concerning the presence of andalusite and cordierite in peraluminous rocks is how they formed, i.e. whether they crystallized from the magma or were trapped as xenocrysts (e.g. Flood and Shaw 1975; Clarke et al. 1976, 2005; Bellido and Barrera 1979; Phillips et al. 1981; Allen and Barr 1983; Weber et al. 1985; Didier and Dupraz 1986; Georget and Fourcade 1988; Clarke 1995; Erdmann et al. 2004; Gottesmann and Förster 2004; Dahlquist et al. 2005). We have focused here on the petrography, mineral chemistry, and the bulk major and trace element composition of the Santa Cruz igneous facies of the La Costa peraluminous granite pluton in the province of La Rioja, NW Argentina, which contains Na- and Li-rich cordierite, andalusite and muscovite. The occurrence of Na-rich cordierite has been reported in some felsic to highly felsic granitoids (SiO₂ >71 wt%, e.g. Erdmann et al. 2004; Villaseca and Barbero 1994). However, the presence of Na-rich cordierite in granitic rocks of relatively low silica contents such as the Santa Cruz igneous facies (SiO₂ = 65.4-68.6 wt%) has not been found in the literature so far. We provide evidence that supports a magmatic origin for these minerals and evaluate the substitution mechanism that led to this distinctive cordierite composition. Crystallization pressure and temperature values for the La Costa pluton have also been estimated to constrain the physical conditions of formation of igneous muscovite, and alusite, and Na- and Li-rich cordierite.

Geological setting and geochemistry of the La Costa pluton

The La Costa pluton is a major igneous body in the northeastern part of the Sierra de Velasco (Alasino et al. 2006). Andalusite and Na- and Li-rich cordierite coexist in the Santa Cruz igneous facies, an alkali-rich peraluminous granite with relatively low silica content (SiO₂ = 65.4–68.6 wt%), which constitutes the northern part of the pluton (Fig. 1). Alasino et al. (2005) provided a first detailed account of the field relationships, petrography and whole-rock chemistry of the Santa Cruz igneous facies. Subsequently, Alasino et al. (2006) recognized two additional granitic igneous facies to the south, the Anjullón and the Anillaco, and proposed that the three igneous facies define a single body, named the La Costa pluton.

The La Costa pluton rocks are two-mica alkali-rich leucocratic monzogranites and alkali feldspar granites, with muscovite always prevalent over biotite, with equigranular texture and medium grain-size (4-5 mm). They have no visible foliation and sharp contacts against Carboniferous porphyritic monzogranites (with Pl-Kfs-Qtz-Bt and Ms-Ap-Mon-Zrn as accessories, abbreviations after Kretz 1983) of the Asha pluton and granitic mylonitic rocks (Pl-Kfs-Qtz-Bt-Ms-Grt) of the Tinogasta-Pituil-Antinaco (TIPA) shear zone (López and Toselli 1993; Höckenreiner et al. 2003; Alasino 2007) (Fig. 1b). Each igneous facies of the La Costa pluton is lithologically homogeneous. The modal data are summarized in Table 1. The Santa Cruz igneous facies is distinguished by the presence of andalusite and Na-and Li-rich cordierite; it has a monzogranitic composition. The Anillaco igneous facies (SiO₂ \sim 74 wt%, monzogranite in composition) is distinguished by containing Mn-rich garnet (spessartine between 42 and 48% of the total molecular composition). The Anjullón igneous facies (SiO₂ ~75 wt%), an alkali-feldspar granite, is characterized by abundant tourmaline and albite (An_{1.1}) (Alasino et al. 2006; Alasino 2007). The parental magmas of La Costa pluton were inferred to have resulted from partial melting of metapelitic protoliths within the TIPA shear zone (Alasino 2007).

The La Costa pluton rocks show relatively high Al₂O₃ (13.82-18.01 wt%), Na₂O (3.45-3.93 wt%), K₂O (3.97-5.99 wt%), P₂O₅ (0.27–0.76 wt%), intermediate to low total iron (1.02-2.28 wt% Fe₂O₃) and low MgO (0.03-0.91 wt%), TiO₂ (0.02–0.27 wt%), MnO (0.05–0.14 wt%) and CaO (0.40-1.17 wt%) (Alasino et al. 2006; Alasino 2007). They are peraluminous, with ASI [molecular Al₂O₃/((CaO- P_2O_5 + Na₂O + K₂O) \geq 1.1, and are distinctively enriched in some trace elements such as Cs (22-162 ppm), Rb (359–778 ppm), Be (4–22 ppm), Bi (2–216 ppm), Li (137– 526 ppm), U (4-27 ppm), Sn (5-43 ppm), W (5-35 ppm), Zn (33-105 ppm), Nb (18-46 ppm), Ga (18-25 ppm) and B (tourmaline in the Anjullón igneous facies can amount to 5 modal %) (Alasino et al. 2006; Alasino 2007). Moreover, they are depleted in Cr, Ni, Co and REE (particularly the Anjullón and the Anillaco igneous facies, $\Sigma REE = 10-18$ and 20-25 ppm, respectively) (Alasino et al. 2006; Alasino 2007). The Santa Cruz facies shows the highest contents of TiO₂, Al₂O₃, FeO, MgO, CaO, K₂O and some trace elements such as Be, Sr, Ba, Zr and REE. Whole-rock chemical analyses of the Santa Cruz igneous facies are summarized in Table 2.

Analytical methods

Petrographic investigations were conducted on 29 samples. Electron microprobe analyses were determined on two selected samples using a JEOL Superprobe JXA-8900-M equipped with five crystal spectrometers at the Luis Brú Electron Microscopy Center, Complutense University, Madrid, Spain. Operating conditions were: acceleration voltage 15 kV, probe current 20 nA, and

Fig. 1 a Geological sketch map of the Sierras Pampeanas showing the location of the Sierra de Velasco (V). **b** Studied area showing location of the La Costa pluton and its igneous facies. *1* Santa Cruz igneous facies, *2* Anjullón igneous facies (Alasino et al. 2006; Alasino 2007). *Dotted line* in the Antinaco magmatic complex corresponds to secondary shear zone

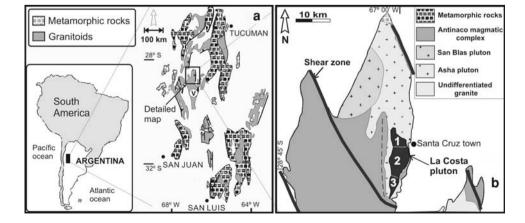


Table 1 Representative modal compositions of the La Costa pluton

| Igneous facies Number of samples Total points | Santa Cruz 4 991 | Anillaco 3 903 | Anjullón 4 815 |
|---|------------------------|----------------------|----------------------|
| Modal % | | | |
| Qtz | 27.6 ± 1.4 | 36.1 ± 0.8 | 43.3 ± 5.5 |
| Kfs | 27.1 ± 1.0 | 18.8 ± 0.9 | 12.6 ± 2.6 |
| Pl | 31.5 ± 0.6 | 31.7 ± 2.6 | 30.9 ± 1.9 |
| Bt | 3.5 ± 1.5 | 2.6 ± 0.6 | 1.9 ± 1.4 |
| Ms | 6.9 ± 1.4 | 7.6 ± 1.1 | 7.2 ± 1.1 |
| Crd | 1.5 ± 0.5 | _ | _ |
| Grt | _ | 2.4 ± 0.9 | - |
| And | 0.3 ± 0.3 | _ | _ |
| Tur | 0.5 ± 0.1 | 0.3 ± 0.1 | 3.3 ± 1.7 |
| Ap | 0.4 ± 0.1 | 0.2 ± 0.0 | 0.5 ± 0.1 |
| Zrn + Mon | 0.4 ± 0.1 | 0.1 ± 0.0 | 0.1 ± 0.0 |
| Opq | 0.3 ± 0.0 | 0.2 ± 0.1 | 0.2 ± 0.1 |

Mineral abbreviations from Kretz (1983)

beam diameter 1-2 µm. Absolute abundances for each element were determined by comparison with known standards (Jarosewich et al. 1980; McGuire et al. 1992), using an on-line ZAF program. Trace elements were determined in Al-rich minerals and micas for two samples using LA-ICP-MS analyses at Granada University, Spain. The LA-ICP-MS analyses were carried out with a Nd-YAG 213 µm Mercantek laser and a torch-shielded quadrupolar Agilent 7500 ICP-MS spectrometer. The laser beam was set a diameter of 60 μ m, with a repetition rate of 10 Hz and output energy of 1 mJ per pulse. The ablation time was 60 s and the spots were pre-abraded for 45 s with laser output energy of 0.3 mJ per pulse; ablation was in a He atmosphere. Every analytical session was started and ended with NIST-610, which was also measured every 6-8 spots. To improve detection limits, blanks (with the laser energy set to zero) were recorded before each spot and subtracted from the analytical signal. Data were reduced using home-made software (freely available from F: Bea) written in STATA programing language (Statacorp 2005). This software permits outliers to be identified and discarded, blank subtraction, drift correction, correction for an external standard and conversion to concentration units on an external standard. The precision, calculated as the coefficient of variation $(100 \times SD/average)$ on ten replicates of NIST-6 measured in every session, was about $\pm 3\%$.

Three samples were chosen for whole-rock chemical analysis, including some major and trace elements (ICP-OES at Alex Stewart Assayers, Argentina SA). In addition, two whole-rock analyses from Alasino et al. (2005) were

 Table 2
 Representative whole rock chemical analyses for the Santa

 Cruz igneous facies (La Costa pluton)

| Sample no. | SVC-1a ^a | SVC-4a ^a | SVC-104 ^b | SVC-105 ^b | SVC-106 ^b |
|--------------------------------|---------------------|---------------------|----------------------|----------------------|----------------------|
| wt% | | | | | |
| SiO_2 | 65.36 | 68.62 | | | |
| TiO ₂ | 0.27 | 0.21 | | | |
| Al_2O_3 | 18.01 | 16.82 | 17.38 | 17.19 | 15.82 |
| Fe ₂ O ₃ | 2.28 | 1.47 | | 2.27 | 2.97 |
| MnO | 0.08 | 0.05 | 0.11 | 0.08 | 0.06 |
| MgO | 0.91 | 0.52 | 0.86 | 0.75 | 0.48 |
| CaO | 1.17 | 0.93 | 1.35 | 1.21 | 0.90 |
| Na ₂ O | 3.45 | 3.52 | 3.49 | 3.57 | 3.22 |
| K ₂ O | 5.67 | 5.99 | 5.51 | 5.70 | 6.00 |
| P_2O_5 | 0.52 | 0.43 | 0.54 | 0.48 | 0.41 |
| LOI | 1.24 | 0.98 | | | |
| Total | 98.96 | 99.54 | | | |
| ppm | | | | | |
| Li | | | 180 | 152 | 137 |
| Be | 22 | 14 | | | |
| Cs | 49.4 | 47.4 | | | |
| Rb | 362 | 359 | | | |
| Sr | 116 | 104 | 123 | 117 | 100 |
| Ba | 517 | 436 | 472 | 466 | 428 |
| Zr | 116 | 95.5 | 101 | 99 | 83 |
| La | 28.4 | 21.1 | 28 | 27 | 22 |
| Ce | 61.9 | 44.9 | | | |
| Pr | 6.85 | 5.07 | | | |
| Nd | 26.4 | 19.8 | | | |
| Sm | 6.32 | 4.69 | | | |
| Eu | 1.25 | 1.10 | | | |
| Gd | 5.53 | 4.24 | | | |
| Tb | 1.05 | 0.79 | | | |
| Dy | 5.49 | 4.28 | | | |
| Но | 0.95 | 0.76 | | | |
| Er | 2.55 | 1.99 | | | |
| Tm | 0.34 | 0.28 | | | |
| Yb | 1.96 | 1.57 | | | |
| Lu | 0.29 | 0.23 | | | |
| ΣREE_{total} | 149 | 111 | | | |
| ASI | 1.42 | 1.30 | 1.35 | 1.31 | 1.27 |

Total iron as Fe_2O_3 . Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, Na_2O and P_2O_5 in SVC-104, 105 and 106 were measured as cations and converted into oxides

^a Data from Alasino et al. (2005) obtained by ICP and ICP-MS at ACTLABS (Canada)

^b Data obtained by ICP-OES at Alex Stewart Assayers Argentina SA

included in this study (ICP and ICP-MS, following the procedure 4-Lithoresearch code at Activation Laboratories, Ontario, Canada).

Mineral texture and chemistry of the Santa Cruz igneous facies

We focus here on the texture and mineral chemistry of andalusite and Na- and Li-rich cordierite of the Santa Cruz igneous facies as well as on biotite and muscovite that probably crystallized in chemical equilibrium with them, and are thus relevant to our interpretation of the crystallization history.

Andalusite

Andalusite is an accessory mineral in the Santa Cruz igneous facies (<0.6 modal %). It is usually found as small (\leq 1.2 mm) irregular relic grains armored by muscovite either polycrystalline or large single plates (Figs. 2a–c, 3a). Former andalusite crystals were euhedral to subhedral prismatic, with still recognizable cleavage and without chiastolite (carbonaceous material) or mineral inclusions. They show pink to colorless pleochroism. According to the textural classification by Clarke et al. (2005) of andalusite in felsic peraluminous igneous rocks, the Santa Cruz andalusite corresponds to the "*single -type*" (Figs. 2, 3), i.e. single andalusite grains with or without muscovite pseudomorphs (either mono or polycrystalline).

Electron microprobe analyses of andalusite are shown in Table 3. Some spot locations are shown in Fig. 3a for illustrative purposes. The compositions are very similar to those reported for other andalusites crystallized from a magma (D'Amico et al. 1981; Gordillo et al. 1985; Kawakami 2002; Clarke et al. 2005), i.e. Al_2O_3 between 62.90 and 64.26 wt%, and small amounts of Fe_2O_3 (0.42–0.51wt%). An anomalously high K_2O value of 0.43 wt% probably resulted from interference with muscovite.

The LA–ICP–MS results are reported in Table 4. Trace element contents are generally low, with Li (except one of 113 ppm), Co, Ni, Cu lower than 1 ppm and Sc, Cr, Zn ranging from 1 to 20 ppm. The REE contents are below

detection limits except for one sample that shows measurable light REE (La, Ce, Pr and Nd). P, Ga, and V contents are high with range: 71–204, 126–168 and 120– 161 ppm, respectively (Table 4; Fig. 4).

Na- and Li-rich cordierite

Cordierite constitutes 1-2% of the mode. It is often found as medium-grained (≤ 2.5 mm) euhedral to subhedral crystals with a few random inclusions of zircon, apatite and opaque minerals (mainly Fe–Ti oxides). Irregular single grains of cordierite are commonly found armored by polycrystalline muscovite, suggesting subsolidus replacement by the latter mineral (Fig. 3b). In some cases, irregular single grains of cordierite are surrounded by muscovite and biotite and by chlorite after biotite (Fig. 2d). Cordierite and andalusite show a homogeneous distribution in thin section.

Cordierite electron microprobe analysis results are shown in Table 5. Some spot locations are shown in Fig. 3b. The Al₂O₃ content (31.64–32.84 wt%) is high relative to other Na-rich cordierites ($1.65 \le Na_2O \le 1.99$ wt% and $28.2 \le Al_2O_3 \le 29.5$ wt%) from pegmatites (Gordillo et al. 1985), but is similar to those from felsic monzogranites (e.g. Villaseca and Barbero 1994; Erdmann et al. 2004). However, the Santa Cruz facies cordierite is remarkably rich in Na₂O (1.55-1.77 wt%), which is unusual for cordierites from granitic rocks of relatively low silica content (i.e. between 65 and 68 wt%). The high MnO content (0.85-1.43 wt%) is also remarkable. Contents of K₂O (0.01-0.04 wt%) and CaO (0.01-0.13 wt%), i.e. elements that enter the hexagonal channels of the structure, are low. The X_{Fe} range (0.39-0.60, mean of 13 analyses = 0.47; Table 5) is similar to the compositional range reported for other Na-rich cordierites (Gordillo et al. 1985).

LA–ICP–MS data for the Santa Cruz facies cordierite are reported in Table 4 and Fig. 4. These cordierites show remarkably high concentrations of Li (654–3,043 ppm),

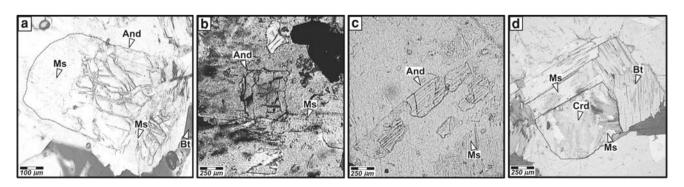
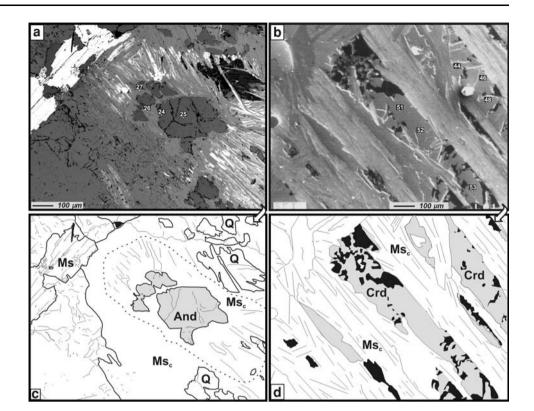


Fig. 2 Photomicrographs showing the textural relationships between andalusite (\mathbf{a} - \mathbf{c}), Na-rich cordierite (\mathbf{d}) and muscovite from Santa Cruz igneous facies, La Costa pluton: abbreviations mineral after Kretz (1983); \mathbf{b} and \mathbf{c} taken from Alasino et al. (2005)

Fig. 3 a, b BSE images with corresponding sketches (c, d) showing the location of electron microprobe spots for andalusite, Na-rich cordierite (Tables 3, 5), muscovite from the Santa Cruz igneous facies and textural relationships among them. According to Clarke et al. (2005), textural relationships like those shown here are indicative of subsolidus replacement of muscovite after andalusite and Na- and Li-rich cordierite that resulted in a polycrystalline muscovite pseudomorph. Mineral abbreviations after Kretz (1983)



Rb (7–678 ppm), Zr (9–463 ppm), Cs (162–442 ppm) and Be (82–1,878 ppm). Other trace element contents are: Zn (85–310 ppm), Ba (10–233 ppm), Cu (5–145 ppm), P (20–104 ppm), Ga (19–59 ppm), Sr (3–48 ppm) and Hf (5–42 ppm). Elements such as Sc, V, Cr, Co, Ni, Ta, Pb, Tl, U, Y, Nb and Th are in most cases well below 15 ppm. The total REE content is low (<19.1 ppm); intermediate and heavy REE contents are in most cases below the detection limit.

Substitution mechanisms in Na- and Li-rich cordierite

Several authors (e.g. London 1995; Černý et al. 1997; Evensen and London 2003; Bertoldi et al. 2004) pointed out that Be and Li can be significantly fractionated in cordierite $(D_{Li}^{Crd/melt} = 125 \pm 3.7 \text{ and } D_{Be}^{Crd/melt} = 29.1 \pm 2.1$; Bea et al. 1994) coincident with coupled Na+ substitution (Gordillo et al. 1985; Schreyer 1985; Bertoldi et al. 2004 and references therein). In fact, the high contents of Li (~0.18 a.p.f.u.) and Na (0.32–0.37 a.p.f.u.) (Table 5) found in cordierite from the Santa Cruz igneous facies correlate well with the low octahedral site occupancy by divalent cations ($\Sigma Mg + Fe^{2+} + Mn = 1.73$ a.p.f.u., average from 13 electron microprobe analyses; Table 5). This evidence suggests that incorporation of Li in cordierite probably resulted from the following coupled substitution (Schreyer 1985) as evidenced in Fig. 5:

$${}^{Ch}Na^{+} + {}^{VI}Li^{+} = {}^{Ch}[] + {}^{VI}Mg^{2+}.$$
(1)

The introduction of Na⁺ in the hexagonal channels of the cordierite crystal structure would involve coupled introduction of Li^+ in the octahedral site, replacing divalent cations. Moreover, the high content of Be in the Santa Cruz facies cordierite (82–1,879 ppm) suggests a coupled substitution (Černý and Povondra 1966) of the type:

$${}^{Ch}Na^{+} + {}^{IV}Be^{2+} = {}^{Ch}[] + {}^{IV}Al^{3+}.$$
 (2)

The high content of Cs in the Santa Cruz facies cordierite (162–442 ppm) is also noticeable. Fractionation of Cs into magmatic cordierite ($D_{Cs}^{Crd/melt} = 31.5 \pm 1.6$; Bea et al. 1994) has in fact been invoked by several authors (e.g. London 1995; Černý et al. 1997; Evensen and London 2003; Bertoldi et al. 2004).

Biotite

Biotite is medium-grained ($\sim 2.8 \times 1.6$ mm) euhedral to subhedral, with light- to dark-brown pleochroism. Occasionally small crystals of zircon, monazite and apatite were observed as inclusions.

In terms of Al^{IV} versus $Fe^{2+}/(Fe^{2+} + Mg)$, biotite from the Santa Cruz igneous facies shows high siderophyllite– eastonite contents and intermediate $Fe^{2+}/(Fe^{2+} + Mg)$ ratios between 0.55 and 0.57 (Table 6). Biotite has a

 Table 3 Representative composition of the Santa Cruz igneous facies and alusite

 Table 4 Representative LA-ICP-MS analyses of the Santa Cruz igneous facies Al-rich minerals

Cordierite 1

Andalusite

Mineral

| Mineral | Andalus | ite 1 | Andalus | ite 2 | | |
|--------------------------------|-----------|------------|------------|------------|--------|--------|
| Analysis no. | 24 | 25 | 59 | 41 | 58 | 60 |
| wt% | | | | | | |
| SiO ₂ | 35.75 | 35.37 | 36.97 | 37.28 | 37.43 | 37.82 |
| Al_2O_3 | 64.26 | 63.21 | 63.87 | 63.64 | 63.65 | 62.90 |
| TiO ₂ | 0.04 | 0.05 | 0.05 | bdl | 0.03 | 0.08 |
| Fe ₂ O ₃ | 0.47 | 0.51 | 0.46 | 0.50 | 0.46 | 0.42 |
| MnO | bdl | 0.01 | bdl | bdl | bdl | bdl |
| MgO | 0.01 | 0.04 | 0.06 | bdl | 0.01 | 0.03 |
| CaO | bdl | 0.01 | 0.01 | bdl | 0.02 | 0.02 |
| Na ₂ O | bdl | bdl | bdl | bdl | bdl | 0.02 |
| K ₂ O | 0.03 | 0.01 | 0.03 | 0.02 | 0.05 | 0.43 |
| F | bdl | 0.03 | bdl | 0.03 | 0.02 | 0.03 |
| Cl | bdl | bdl | bdl | bdl | bdl | 0.01 |
| Total | 100.56 | 99.24 | 101.45 | 101.47 | 101.67 | 101.76 |
| Structural for | mulae cal | culated of | on the bas | is of 20 C |) | |
| Si | 3.85 | 3.86 | 3.94 | 3.97 | 3.98 | 4.03 |
| Al | 8.15 | 8.13 | 8.02 | 7.99 | 7.97 | 7.89 |
| Ti | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Fe ³⁺ | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.03 |
| Mn | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Mg | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Κ | 0.03 | 0.01 | 0.02 | 0.05 | 0.03 | 0.43 |

Total iron measured as FeO and expressed as Fe₂O₃. Andalusite 1 and 2 correspond to different analyzed mineral grains

bdl below detection limit

consistently high Al^{IV} content (2.56–2.66 a.p.f.u.; Table 6). The LA–ICP–MS analyses of biotite reveal high concentrations of Li (609–1,032 ppm), Cs (44–877 ppm), Zn (260–673 ppm), V (49–407 ppm) and Nb (96–313 ppm), with lower concentrations of Cr (\leq 136 ppm), Ga (\leq 64 ppm), Ta (\leq 58 ppm), Sc (\leq 33 ppm), Co (\leq 31 ppm), Ni (\leq 26 ppm), Tl (\leq 11 ppm), Be (\leq 8 ppm), Pb (\leq 4 ppm) and low concentrations of Cu, U, Th, Hf (\leq 2 ppm; Table 7; Fig. 4). The REE total content is low (<8.7 ppm; Table 7).

Muscovite

Care was taken to distinguish between primary and secondary muscovite. Primary muscovite is widely held to be an indicator of peraluminous magmas (Speer 1984). Petrographic evidence and chemical data suggest that both types of muscovite are present in the Santa Cruz igneous facies.

Chemical analyses of texturally primary muscovite (see Table 6), i.e. medium-grained $\sim 3.2 \times 1.9$ mm, euhedral

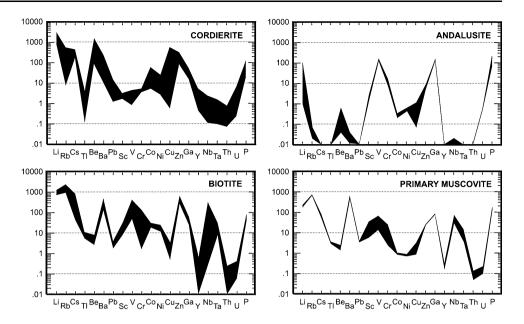
| 23 | 24 | 25 | 7 | 8 | 31 | 32 |
|------|--|---|--|--|--|--|
| | | | | | | |
| 0.95 | 1.01 | 113 | 3,042 | 2,978 | 1,236 | 654 |
| bdl | 0.04 | 0.64 | 205 | 1,878 | 82.0 | 86.5 |
| bdl | bdl | bdl | 161 | 229 | 442 | 281 |
| 132 | 204 | 71.2 | 18.9 | 103 | 94.5 | 49.1 |
| 2.93 | 2.39 | 1.38 | 2.34 | 2.23 | 3.21 | 1.75 |
| 160 | 160 | 119 | 0.85 | 0.90 | 4.38 | 1.93 |
| 7.57 | 16.9 | 18.3 | 5.66 | bdl | 3.76 | bdl |
| 0.36 | 0.30 | 0.21 | 9.88 | 4.64 | 15.0 | 8.40 |
| 0.44 | 0.67 | 0.46 | 2.88 | 4.23 | 11.8 | 4.28 |
| 0.13 | 0.07 | 0.13 | 0.62 | 4.96 | 144 | 20.2 |
| 8.95 | 9.79 | 5.28 | 171 | 84.7 | 310 | 238 |
| 167 | 163 | 125 | 51.9 | 58.9 | 16.8 | 43.8 |
| 0.07 | 0.02 | bdl | 7.44 | 146 | 413 | 678 |
| bdl | bdl | bdl | 3.41 | 8.75 | 48.4 | 10.7 |
| bdl | bdl | bdl | 0.45 | 0.72 | 5.80 | 1.06 |
| bdl | 0.03 | 0.14 | 13.0 | 8.67 | 462 | 64.3 |
| bdl | 0.02 | bdl | 0.13 | 0.11 | 2.36 | 0.66 |
| | 0.04 | 0.02 | 10.0 | | 163 | 232 |
| | | | | | | 5.15 |
| bdl | | | bdl | bdl | | 0.24 |
| bdl | | | 0.11 | 1.25 | | 4.69 |
| | | | | | | 4.77 |
| | | | | | | 0.07 |
| | | | | | | 1.20 |
| | | | | | | |
| bdl | bdl | 0.17 | 0.08 | bdl | 3.83 | 0.84 |
| | | | | | | 1.42 |
| | | | | | | 0.17 |
| | | | | | | 0.74 |
| | | | | | | 0.07 |
| | | | | | | 0.10 |
| | | | | | | 0.07 |
| | | | | | | bdl |
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| | | | | | | bdl |
| | | | | | | bdl |
| | 0.95 bdl 132 2.93 160 7.57 0.36 0.44 0.13 8.95 167 0.07 bdl bdl bdl bdl bdl bdl | 0.9551.01bdl0.04bdlbdl1322042.932.391601607.5716.90.360.300.440.670.130.078.959.791671630.070.02bdlbdlbdl0.03bdl | 0.951.01113bdl0.040.64bdlbdlbdl13220471.22.932.391.381601601197.5716.918.30.360.300.210.440.670.460.130.070.138.959.795.281671631250.070.02bdlbdlbdlbdlbdl0.030.14bdl0.040.02bdl< | 0.951.011133,042bdl0.040.64205bdlbdlbdl16113220471.218.92.932.391.382.341601601190.857.5716.918.35.660.360.300.219.880.440.670.462.880.130.070.130.628.959.795.2817116716312551.90.070.02bdl7.44bdlbdlbdl0.45bdl0.030.1413.0bdl0.02bdl0.13bdlbdlbdl0.13bdlbdlbdl0.11bdlbdlbdl0.12bdlbdlbdl0.17bdlbdlbdl0.12bdlbdl0.020.13bdlbdlbdl0.17bdlbdlbdl0.17bdlbdl0.120.10bdlbdl0.120.10bdlbdl0.120.10bdlbdl0.120.13bdlbdl0.140.12bdlbdl0.140.12bdlbdl0.140.12bdlbdl0.140.12bdlbdlbdlbdlbdlbdlbdlbdlbdlbdlb | 0.951.011133.0422.978bdl0.040.642051,878bdlbdlbdl16122913220471.218.91032.932.391.382.342.231601601190.850.907.5716.918.35.66bdl0.360.300.219.884.640.440.670.462.884.230.130.070.130.624.968.959.795.2817184.716716312551.958.90.070.02bdl7.44146bdlbdlbdl0.450.72bdlbdlbdl0.450.72bdl0.030.1413.08.67bdl0.02bdl0.130.11bdlbdlbdl0.130.11bdlbdlbdl0.02bdlbdlbdlbdl0.130.12bdlbdlbdl0.130.12bdlbdlbdl0.170.12bdlbdlbdl0.170.12bdlbdlbdl0.170.12bdlbdlbdl0.170.12bdlbdl0.170.130.67bdlbdl0.141.070.13bdlbdl0.160.77bdlbdlbdl </td <td>0.95 1.01 113 3,042 2,978 1,236 bdl 0.04 0.64 205 1,878 82.0 bdl bdl bdl 161 229 442 132 204 71.2 18.9 103 94.5 2.93 2.39 1.38 2.34 2.23 3.21 160 160 119 0.85 0.90 4.38 7.57 16.9 18.3 5.66 bdl 3.76 0.36 0.30 0.21 9.88 4.64 15.0 0.44 0.67 0.46 2.88 4.23 11.8 0.13 0.07 0.13 0.62 4.96 144 8.95 9.79 5.28 171 84.7 310 167 163 125 51.9 58.9 16.8 0.07 0.02 bdl 0.45 0.72 5.80 bdl bdl 0.13 0.11</td> | 0.95 1.01 113 3,042 2,978 1,236 bdl 0.04 0.64 205 1,878 82.0 bdl bdl bdl 161 229 442 132 204 71.2 18.9 103 94.5 2.93 2.39 1.38 2.34 2.23 3.21 160 160 119 0.85 0.90 4.38 7.57 16.9 18.3 5.66 bdl 3.76 0.36 0.30 0.21 9.88 4.64 15.0 0.44 0.67 0.46 2.88 4.23 11.8 0.13 0.07 0.13 0.62 4.96 144 8.95 9.79 5.28 171 84.7 310 167 163 125 51.9 58.9 16.8 0.07 0.02 bdl 0.45 0.72 5.80 bdl bdl 0.13 0.11 |

Cordierite 1 and 2 correspond to different analyzed mineral grains *bdl* below detection limit

crystals, plot in the expected compositional field on a Mg– Ti–Na diagram (Fig. 6a) according to the criteria of Miller et al. (1981). Moreover, primary muscovite in the Santa

Cordierite 2

Fig. 4 Absolute abundance plots of trace element contents (ppm) other than REE in cordierite, andalusite, biotite and primary muscovite from the Santa Cruz igneous facies, La Costa pluton



Cruz facies is similar in composition to that coexisting with aluminous minerals (Fig. 6a). The LA–ICP–MS analyses of primary muscovite show relatively high contents of Li (183–221 ppm) and P (103–137 ppm), intermediate contents of Ga (79–86 ppm), Cs (55–88 ppm), Nb (29–77 ppm), V (17–69 ppm) and Zn (24–26 ppm) (Table 8). A few elements such as the transition metals (Sc, Cu, Zr and Ta), Be, Tl and Pb show contents ranging from 1 to 15 ppm. The remaining elements reported in Table 8 (i.e. Ni, Y, Hf, Th and U) are below 1 ppm (see Fig. 4). Total REE content is low (<5.82 ppm; Table 8).

Secondary muscovite is of two types: (1) medium to finegrained (~1.1 × 0.6 mm) anhedral (Ms_b), grown from biotite or K-feldspar and, (2) polycrystalline (Ms_c), as pseudomorphs and overgrowths after andalusite and/or Na- and Li-rich cordierite (Figs. 2, 3). Electron microprobe analyses of Ms_{b-c} are shown in Table 6. Secondary muscovite plots in the secondary-mica field of the Mg–Ti–Na diagram (Fig. 6a). Trace element contents in secondary muscovite Ms_c embrace those of primary muscovite (Table 8; Fig. 6b). Relative to primary muscovite, secondary muscovite after cordierite shows lower contents of P, Sc, V, Cr, Y, Nb, Ta, Th and U (Fig. 6b), whereas secondary muscovite after andalusite shows higher contents of those elements than primary muscovite (Fig. 6b). REE content in secondary muscovite is below detection limit (Table 8).

Physical conditions of crystallization of the Santa Cruz igneous facies

Physical conditions of crystallization of the La Costa pluton were determined for the Anillaco igneous facies, which contains Mn-rich garnet (Sps \sim 46 mol %, see previous

section). This granite is similar to other Mn-rich garnet granites (e.g. Dahlquist et al. 2007 and references therein). Anderson (1996) provided relevant recommendations for the use of mineral thermometers and barometers in igneous rocks and concluded that the Ganguly and Saxena (1984) geothermometer, using the $Fe^{2+} + Mg$ partition between garnet and biotite, is the most robust to account for the effects of high Mn, when CaO < 10%. For this reason the Ganguly and Saxena (1984) Fe²⁺-Mg²⁺ garnet-biotite exchange geothermometer and the R2 and R4 geobarometers of Hoisch (1990) were combined to obtain P-T values that can extrapolated to the Santa Cruz igneous facies, particularly pressure. Both gauges require equilibrium crystallization of quartz, garnet, biotite, muscovite and plagioclase. Because both calibrations are P-T dependent, an iterative procedure was followed. The resultant values ($T \sim 730^{\circ}$ C, and $P \sim 1.9$ kbar; Table 9) are consistent with crystallization of Mn-rich garnet and biotite under magmatic conditions (e.g. Clemens and Wall 1981; Miller and Stoddard 1981). The zircon saturation temperature (T_{Zr}) calculated from the bulk-rock composition of the Santa Cruz igneous facies using the equation of Miller et al. (2003), is 758°C (Table 9), consistent with that of the Anillaco igneous facies.

Discussion

Evidence for a magmatic origin of andalusite and cordierite

The Santa Cruz facies andalusite and cordierite cannot be interpreted either as part of a restite assemblage resulting from partial melting of a metamorphic protolith (e.g. Flood and Shaw 1975; Zeck and Williams 2002) or as xenocrysts

Table 5 Representative microprobe analyses of the Santa Cruz igneous facies cordierite

| Mineral | Cordier | rite 1 | Cordier | Cordierite 2 | | | | | | | | | | $\operatorname{Crd}^{\operatorname{a}}$ |
|--------------------------------|-----------|------------|-----------|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---|
| Analysis no. | 30 | 31 | 44 | 44′ | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 54 | Av. |
| wt% | | | | | | | | | | | | | | |
| SiO ₂ | 47.49 | 47.61 | 47.01 | 46.82 | 47.05 | 47.50 | 46.88 | 48.18 | 47.58 | 46.12 | 47.45 | 48.04 | 48.10 | 47.37 |
| Al_2O_3 | 32.82 | 32.67 | 31.97 | 31.74 | 32.49 | 32.54 | 32.23 | 32.18 | 32.72 | 31.64 | 32.92 | 32.68 | 32.68 | 32.41 |
| TiO ₂ | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | 0.04 | 0.01 | 0.02 | 0.03 | bdl | 0.01 |
| FeO | 7.01 | 6.85 | 9.88 | 9.86 | 9.95 | 7.27 | 6.98 | 6.49 | 9.63 | 9.00 | 7.57 | 6.69 | 6.76 | 8.00 |
| MnO | 0.90 | 1.38 | 0.89 | 0.95 | 0.85 | 1.29 | 1.43 | 1.43 | 0.97 | 1.27 | 0.92 | 1.21 | 0.97 | 1.11 |
| MgO | 5.82 | 5.77 | 4.08 | 3.71 | 4.27 | 5.42 | 5.34 | 5.70 | 4.41 | 4.44 | 5.34 | 5.60 | 5.85 | 5.06 |
| CaO | 0.01 | 0.04 | 0.08 | 0.05 | 0.13 | 0.07 | 0.11 | 0.07 | 0.07 | 0.10 | 0.03 | 0.06 | 0.05 | 0.07 |
| Na ₂ O | 1.58 | 1.55 | 1.67 | 1.64 | 1.74 | 1.64 | 1.76 | 1.75 | 1.70 | 1.77 | 1.65 | 1.70 | 1.63 | 1.68 |
| K ₂ O | 0.01 | bdl | 0.04 | bdl | 0.04 | bdl | 0.03 | 0.01 | bdl | 0.01 | bdl | 0.01 | 0.03 | 0.01 |
| F | bdl | bdl | bdl | 0.01 | bdl | bdl | bdl | bdl | bdl | 0.01 | bdl | bdl | bdl | bdl |
| Cl | bdl | bdl | bdl | bdl | bdl | 0.01 | bdl | bdl | bdl | 0.01 | bdl | bdl | bdl | bdl |
| Li ₂ O ^b | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 0.43 |
| BeO ^b | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 0.16 |
| Total | 95.64 | 95.87 | 95.62 | 94.78 | 96.52 | 95.74 | 94.76 | 95.81 | 97.12 | 94.38 | 95.90 | 96.02 | 96.07 | 96.30 |
| Structural formu | lae calcu | lated on t | the basis | of 18 O | | | | | | | | | | |
| Si | 5.03 | 5.04 | 5.05 | 5.08 | 5.02 | 5.04 | 5.03 | 5.09 | 5.03 | 5.02 | 5.03 | 5.07 | 5.07 | 5.01 |
| $\mathrm{Al}^{\mathrm{IV}}$ | 3.97 | 3.96 | 3.95 | 3.92 | 3.98 | 3.96 | 3.97 | 3.91 | 3.97 | 3.98 | 3.97 | 3.93 | 3.93 | 3.95 |
| Be | | | | | | | | | | | | | | 0.04 |
| Sum-T | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.00 | 9.000 |
| $\mathrm{Al}^{\mathrm{VI}}$ | 0.13 | 0.11 | 0.10 | 0.13 | 0.09 | 0.12 | 0.11 | 0.10 | 0.11 | 0.08 | 0.13 | 0.13 | 0.12 | 0.16 |
| Ti | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Fe ²⁺ | 0.62 | 0.61 | 0.89 | 0.89 | 0.89 | 0.65 | 0.63 | 0.57 | 0.85 | 0.82 | 0.67 | 0.59 | 0.60 | 0.62 |
| Mn | 0.08 | 0.12 | 0.08 | 0.09 | 0.08 | 0.12 | 0.13 | 0.13 | 0.09 | 0.12 | 0.08 | 0.11 | 0.09 | 0.08 |
| Mg | 0.92 | 0.91 | 0.65 | 0.60 | 0.68 | 0.86 | 0.85 | 0.90 | 0.69 | 0.72 | 0.84 | 0.88 | 0.92 | 0.92 |
| Li | | | | | | | | | | | | | | 0.18 |
| Sum-B | 1.75 | 1.75 | 1.72 | 1.71 | 1.74 | 1.75 | 1.72 | 1.70 | 1.74 | 1.74 | 1.72 | 1.71 | 1.73 | 1.96 |
| Ca | 0.00 | 0.00 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 |
| Na | 0.32 | 0.32 | 0.35 | 0.34 | 0.36 | 0.34 | 0.37 | 0.36 | 0.35 | 0.37 | 0.34 | 0.35 | 0.33 | 0.33 |
| К | 0.00 | 0.000 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Sum-A | 0.32 | 0.32 | 0.37 | 0.35 | 0.39 | 0.35 | 0.38 | 0.37 | 0.36 | 0.38 | 0.34 | 0.36 | 0.34 | 0.33 |
| Fe/(Fe + Mg) | 0.40 | 0.40 | 0.58 | 0.60 | 0.57 | 0.43 | 0.42 | 0.39 | 0.55 | 0.53 | 0.44 | 0.40 | 0.39 | 0.47 |

Total iron measured as FeO. Cordierite 1 and 2 correspond to different analyzed mineral grains

bdl below detection limit; nd not determined

^a Corresponds to the average of the analysis of cordierite using the data obtained from electron microprobe (this table) and the data obtained from LA–ICP–MS (Table 4)

^b Data obtained from the average of Li and Be from Table 4 and converted into oxides

added to the magma from metamorphic country rock (e.g. Ugidos and Recio 1993; Stimac et al. 1995; Gottesmann and Förster 2004).

 Field evidence Andalusite and cordierite were only found in the Santa Cruz igneous facies, i.e. they are absent in the other two igneous facies of the La Costa pluton, suggesting that both minerals crystallized from the Santa Cruz facies magma. The La Costa pluton was emplaced within undeformed biotite porphyritic granites of the Asha pluton and granitic mylonites of the Antinaco magmatic complex (Fig. 1b). Moreover, metamorphic rocks are not found in the area and metamorphic xenoliths are absent from all three facies of the La Costa pluton (Fig. 1b). Thus, there is no field evidence for a local metamorphic origin of andalusite and cordierite.

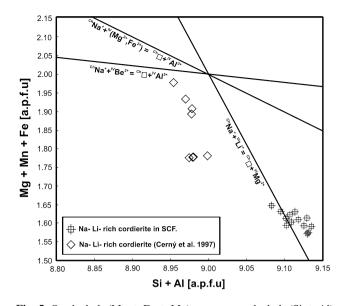


Fig. 5 Octahedral (Mg + Fe + Mn) versus tetrahedral (Si + Al) site occupancy for natural cordierite, ignoring Li and Be in formula calculations (modified from Bertoldi et al. 2004). *SCF* Santa Cruz igneous facies

- 2. Textural evidence The primary texture of both minerals is masked by subsolidus replacement and overgrowth of andalusite and cordierite by muscovite. However, when these minerals are well preserved, they show features typical of igneous crystallization (Erdmann et al. 2004; Clarke et al. 2005), i.e. subhedral to euhedral shapes as opposed to allotriomorphic blastic cordierite, few or no mineral inclusions, absence of chiastolite inclusion in the andalusite, grain-size compatible with the magmatic rock-forming minerals of the Santa Cruz igneous facies, and appearance as homogeneously distributed isolated crystals (surrounded by muscovite). Remarkably, no peritectic texture such as reaction rims on Al-rich minerals (e.g. garnet) or inclusions of high grade metamorphic minerals such as sillimanite were found.
- Mineral chemistry Major element compositions of 3. andalusite provide little information on the mineral origin. However, some information can be gained by checking for chemical equilibrium with other minerals (e.g. biotite, muscovite). The consistently high Al^IV content of biotite in all the samples from the Santa Cruz igneous facies is consistent with crystallization in equilibrium with other Al-rich minerals such as andalusite, cordierite and muscovite, a circumstance well-known from other peraluminous rocks with magmatic cordierite or andalusite (e.g. Clarke et al. 2005; Dahlquist et al. 2005). On the other hand, the high Na₂O and MnO contents of the Santa Cruz facies cordierite (Table 5) are remarkable and consistent with a magmatic origin (e.g. Gordillo et al. 1985; Secchi

| micas | | | | |
|-------------------|-----------------|-----------------|-----------------|-----------------|
| Mineral | Biotite | Muscovite | | |
| Textural type | | Msa | Ms _b | Ms _c |
| Analysis no. | Av. $(n = 5)$ | Av. $(n = 3)$ | 33 | Av. $(n = 2)$ |
| wt% | | | | |
| SiO ₂ | 35.09 ± 0.28 | 45.24 ± 0.31 | 45.04 | 45.76 ± 0.10 |
| TiO ₂ | 2.42 ± 0.27 | 0.26 ± 0.13 | bdl | 0.04 ± 0.02 |
| Al_2O_3 | 19.57 ± 0.10 | 36.09 ± 0.26 | 36.58 | 36.28 ± 0.09 |
| FeO | 18.96 ± 0.40 | 1.03 ± 0.10 | 1.21 | 0.94 ± 0.21 |
| MnO | 0.52 ± 0.02 | 0.03 ± 0.02 | 0.02 | 0.01 ± 0.01 |
| MgO | 8.22 ± 0.12 | 0.76 ± 0.05 | 0.73 | 0.74 ± 0.05 |
| CaO | 0.02 ± 0.02 | 0.02 ± 0.02 | 0.02 | 0.02 ± 0.00 |
| Na ₂ O | 0.08 ± 0.03 | 0.54 ± 0.07 | 0.46 | 0.44 ± 0.03 |
| K ₂ O | 9.60 ± 0.17 | 10.77 ± 0.06 | 10.90 | 10.98 ± 0.19 |
| F | 0.27 ± 0.05 | 0.06 ± 0.05 | 0.02 | 0.03 ± 0.03 |
| Cl | 0.04 ± 0.01 | 0.00 | 0.02 | bdl |
| Total | 94.81 ± 0.68 | 94.77 ± 0.73 | 95.00 | 95.21 ± 0.45 |
| O_F_Cl | 0.12 ± 0.02 | 0.02 ± 0.02 | 0.01 | 0.02 ± 0.01 |
| CTotal | 94.69 ± 0.67 | 95.38 ± 0.69 | 94.99 | 95.20 ± 0.43 |
| Structural formu | ulae calculated | on the basis of | 22 O | |
| Si | 5.39 ± 0.05 | 6.06 ± 0.01 | 6.03 | 6.10 ± 0.00 |
| Al^{IV} | 2.61 ± 0.05 | 1.94 ± 0.01 | 1.97 | 1.90 ± 0.00 |
| Sum-T | 8.00 | 8.00 | 8.00 | 8.00 |
| Al^{VI} | 0.93 ± 0.06 | 3.76 ± 0.03 | 3.80 | 3.79 ± 0.03 |
| Ti | 0.28 ± 0.03 | 0.03 ± 0.01 | 0.00 | 0.00 |
| Fe ²⁺ | 2.44 ± 0.05 | 0.12 ± 0.01 | 0.14 | 0.10 ± 0.02 |
| Mn | 0.07 ± 0.00 | 0.00 | 0.00 | 0.00 |
| Mg | 1.88 ± 0.02 | 0.15 ± 0.01 | 0.15 | 0.15 ± 0.01 |
| Sum-B | 5.60 | 4.06 | 4.09 | 4.04 |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 |
| Na | 0.02 ± 0.01 | 0.14 ± 0.02 | 0.12 | 0.11 ± 0.01 |
| K | 1.88 ± 0.02 | 1.84 ± 0.02 | 1.86 | 1.87 ± 0.03 |
| Sum-A | 1.90 | 1.98 | 1.98 | 1.98 |
| CF | 0.26 ± 0.05 | 0.05 ± 0.04 | 0.02 | 0.03 ± 0.02 |
| CCl | 0.02 ± 0.01 | 0.00 | 0.01 | 0.00 |
| Fe/(Fe + Mg) | 0.56 ± 0.01 | 0.43 ± 0.02 | 0.48 | 0.41 ± 0.04 |

Total iron measured as FeO. Muscovite "a" and "b, c" (subscripts) correspond to primary and secondary muscovite, respectively (see text). Abbreviations mineral after Kretz (1983)

bdl below detection limit

et al. 1991; Villaseca and Barbero 1994; Černý et al. 1997; Rapela et al. 2002; Erdmann et al. 2004; Dahlquist et al. 2005).

Trace elements provide complementary information on the origin of the minerals, particularly for the case of cordierite (e.g. Bea et al. 1994). The high Li content of the Santa Cruz facies cordierite suggests that this mineral crystallized from a Li-enriched magma. Moreover, chemical equilibrium of cordierite with **Table 7** Representative LA–ICP–MS analyses of the SantaCruz igneous facies biotite

| Mineral | Biotite | 1 | | Biotite | 2 | Biotite | Biotite 3 Biotite 4 | | |
|--------------|---------|-------|-------|---------|------|---------|---------------------|-------|------|
| Analysis no. | 1 | 2 | 3 | 19 | 20 | 26 | 27 | 34 | 35 |
| ppm | | | | | | | | | |
| Li | 739 | 674 | 609 | 628 | 636 | 903 | 903 | 1,032 | 956 |
| Be | 4.12 | 3.49 | 3.05 | 2.74 | 3.54 | 4.44 | 5.03 | 8.48 | 6.50 |
| Cs | 876 | 700 | 639 | 44.0 | 55.5 | 178 | 93.0 | 754 | 304 |
| Р | 88.3 | 77.3 | 71.2 | 55.2 | 47.0 | 42.2 | 46.2 | 82.9 | 64.4 |
| Sc | 12.4 | 9.49 | 8.16 | 27.6 | 32.6 | 16.6 | 24.2 | 8.54 | 10.8 |
| V | 70.1 | 57.5 | 48.6 | 347 | 407 | 388 | 347 | 63.2 | 150 |
| Cr | 2.38 | 3.06 | 1.79 | 132 | 136 | 76.8 | 99.3 | 2.84 | 28.8 |
| Co | 22.8 | 19.5 | 17.1 | 20.0 | 18.7 | 31.2 | 30.4 | 23.3 | 24.5 |
| Ni | 14.8 | 12.1 | 11.5 | 15.4 | 14.5 | 24.9 | 26.4 | 15.0 | 14.6 |
| Cu | 1.82 | 1.34 | 1.65 | 2.18 | 3.78 | 0.62 | 3.48 | 0.84 | 0.50 |
| Zn | 409 | 350 | 310 | 312 | 259 | 673 | 650 | 605 | 585 |
| Ga | 37.8 | 32.7 | 29.7 | 37.0 | 33.8 | 64.0 | 57.5 | 34.4 | 26.7 |
| Rb | 1,666 | 1,531 | 1,355 | 943 | 925 | 2,243 | 2,135 | 2,009 | 2,41 |
| Sr | 3.96 | 4.71 | 5.61 | 7.22 | 5.09 | 0.65 | 0.97 | 0.90 | 0.75 |
| Y | 0.54 | 0.59 | 0.71 | 0.50 | 0.68 | 0.03 | 0.04 | 0.10 | bdl |
| Zr | 17.0 | 18.7 | 23.2 | 16.2 | 23.6 | 0.34 | 2.09 | 3.67 | 1.22 |
| Nb | 110 | 96.3 | 88.0 | 107 | 105 | 261 | 213 | 126 | 312 |
| Ba | 174 | 166 | 172 | 157 | 111 | 523 | 361 | 494 | 110 |
| Hf | 0.12 | 0.23 | 0.03 | 0.46 | 0.62 | 0.08 | 0.12 | 0.09 | 0.10 |
| Та | 13.9 | 17.5 | 15.8 | 7.49 | 7.22 | 24.4 | 28.6 | 30.2 | 58.1 |
| Tl | 10.6 | 9.77 | 8.16 | 5.92 | 6.32 | 11.3 | 10.7 | 10.0 | 10.5 |
| Pb | 3.98 | 3.61 | 3.86 | 4.10 | 4.14 | 3.05 | 3.35 | 1.95 | 1.84 |
| Th | 0.21 | 0.24 | 0.26 | 0.20 | 0.23 | bdl | bdl | 0.03 | bdl |
| U | 0.37 | 0.35 | 0.43 | 0.25 | 0.41 | 0.05 | 0.19 | 0.04 | 0.06 |
| REE (ppm) | | | | | | | | | |
| La | 0.67 | 1.02 | 0.12 | 0.64 | 0.87 | 0.14 | 0.04 | 0.09 | 0.04 |
| Ce | 0.79 | 1.10 | 0.15 | 1.14 | 1.35 | 0.21 | 0.04 | 0.10 | 0.06 |
| Pr | 1.02 | 1.47 | 0.18 | 0.11 | 0.15 | 0.03 | bdl | bdl | bdl |
| Nd | 0.45 | 0.55 | 0.05 | 0.48 | 0.67 | 0.04 | 0.02 | 0.09 | bdl |
| Sm | 0.32 | 0.50 | 0.07 | 0.13 | 0.10 | bdl | bdl | bdl | bdl |
| Eu | 2.19 | 3.55 | 0.38 | 0.04 | 0.02 | bdl | bdl | bdl | bdl |
| Gd | 0.31 | 0.46 | 0.02 | 0.08 | 0.11 | bdl | bdl | 0.02 | 0.02 |
| Tb | 0.52 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Dy | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | 0.03 |
| Но | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Er | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Tm | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Yb | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |
| Lu | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl |

Biotite 1, 2, 3 and 4 correspon to different analyzed mineral grains *bdl* below detection limit

> andalusite, biotite and primary muscovite in a magma is also suggested by the fact that the four minerals show high contents of trace elements such as Li, Rb, Cs, Zn, Ga and V.

4. *Whole-rock chemistry* The high ASI values (1.27–1.42; Table 2) of the Santa Cruz igneous facies suggest that the granitic magma was saturated in alumina, making

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precipitation of single cotectic grains of cordierite and andalusite highly probable (D'Amico et al. 1981; Gordillo et al. 1985; Clarke 1995; Dahlquist et al. 2005; Clarke et al. 2005 and references therein). In addition, Patiño Douce (1992) has shown that the activity coefficient of Al in silicic melts is a function of the alkali content of the melt, whereby alkali-rich

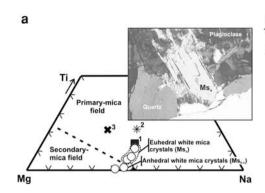
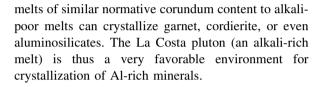


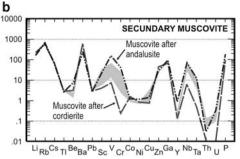
Fig. 6 a Mg–Ti–Na diagram to distinguish between secondary and primary muscovite (Miller et al. 1981). The photomicrograph shows a primary muscovite crystal (Ms_a). b Absolute abundance plots of trace elements other than REE in secondary muscovite formed from andalusite and cordierite (average from Table 8). The gray field



Crystallization conditions of Al-rich minerals

Primary muscovite and andalusite

Curve SCF in Fig. 7 is the inferred P-T path for the Santa Cruz igneous facies. According to this curve, the muscovite in the Santa Cruz igneous facies should be subsolidus if the generally accepted P-T locations of the wet granite solidus and the equilibrium curve for the reaction Ms + Qtz =Kfs + Al-silicates + H_2O (e.g. Pattison and Tracy 1991) are correct (curves 1 and Ms; Fig. 7). This however contradicts growing evidence for late magmatic muscovite in many moderate-depth ($\sim 1-2$ kbar) intrusions (e.g. Dahlquist et al. 2005 and references therein). Moreover, textural and chemical evidence presented here points to a primary origin for some of the muscovites in the Santa Cruz igneous facies. It is well known that addition of P, Li, F and B to peraluminous magmas depresses the granite solidus to lower temperatures at any given pressure (Clarke et al. 2005 and reference therein). The presence of some tourmaline (ca. 0.5 modal %), along with contents of P_2O_5 (ca. 0.50 wt%) and Li (152-180 ppm), and of some F (inferred from the F content of biotite and fluor-apatite) (Tables 2, 6), suggest that the Santa Cruz granitoid solidus was slightly depressed. However, a more important factor for primary muscovite crystallization is the depressing effect on the solidus due to excess Al_2O_3 (~30°C at 2 kbar; Johannes and Holtz 1996) (curve 2; Fig. 7). In fact the



corresponds to the primary muscovite from the Santa Cruz igneous facies. References: *1* average muscovite from plutonic rocks with andalusite (Clarke et al. 2005), *2* average muscovite from Tuaní Granite (Dahlquist et al. 2005) and *3* average muscovite from Peñón Rosado Granite (Dahlquist et al. 2007)

Santa Cruz igneous facies has a very high Al_2O_3 content (up to 18 wt%). On the basis of petrographic and geological data, D'Amico et al. (1981) proposed an empirical extension of the muscovite stability field (Ms + Qtz = Kfs + Al-silicates + H₂O/Melt) in water-undersaturated peraluminous granitic melts (curve Ms'; Fig. 7); together with depression of the solidus resulting from coupled Al saturation and fluxing elements; this would permit muscovite crystallization at a pressure of ca. 2 kbar for magmatic temperatures of ca. 700°C (Fig. 7).

According to the andalusite-sillimanite equilibrium curve of Pattison (1992), at temperatures close to the wet granite solidus-at moderate to low pressure-andalusite is the stable form over a relatively large igneous P-T field (Fig. 7; curves 1 and P92—field A) (e.g. Cesare et al. 2003; Larson and Sharp 2003). However, the latter field decreases significantly if the andalusite-sillimanite equilibrium curve of Holdaway and Mukhopadhyay (1993) is considered, even compared with the Al₂O₃-saturated granite solidus (Johannes and Holtz 1996) (field B, Fig. 7). Grambling and Williams (1985) showed that small amounts of Fe³⁺ and/or Mn³⁺ in andalusite shift the andalusite-sillimanite boundary significantly upwards. For the case of the Santa Cruz facies and alusite with Fe₂O₃ contents between 0.42 and 0.51 wt% (Table 3), a shift of 13°C has been applied to the HM93 and P92 curves (Fig. 7, HM' and P' respectively), values estimated from Kerrick and Speer (1988). However, and alusite can only crystallize to the right of the Ms curve (i.e. the peritectic involving aluminium silicate and muscovite) which implies pressures well below those estimated for the Santa Cruz igneous facies. In consequence the andalusite-sillimanite boundary HM93 for our example seems unrealistic. The andalusite-sillimanite boundary P92 of Pattison (1992), particularly if corrected for the Fe^{3+} content of

Table 8 Representative LA-ICP-MS analyses of the Santa Cruz igneous facies muscovite

| Mineral | Primar | y muscovit | te | | Secondary muse | covite | | | | | |
|--------------|--------|------------|--------|-------------|----------------|--------------|---------------|---------------|---------------|--|--|
| | Musco | vite 1 | Muscov | Muscovite 2 | | | | | | | |
| Analysis no. | 4 | 5 | 14 | 15 | 28, after And | 9, after Crd | 10, after Crd | 29, after Crd | 30, after Crd | | |
| ppm | | | | | | | | | | | |
| Li | 221 | 182 | 203 | 220 | 169 | 403 | 170 | 176 | 174 | | |
| Be | 2.44 | 1.46 | 2.53 | 2.11 | 7.61 | 5.19 | 2.52 | 2.66 | 2.40 | | |
| Cs | 88.1 | 55.0 | 70.8 | 74.1 | 77.7 | 128 | 38.6 | 64.5 | 55.8 | | |
| Р | 122 | 103 | 114 | 137 | 196 | 91.9 | 126 | 93.0 | 79.2 | | |
| Sc | 36.3 | 5.88 | 8.27 | 7.69 | 22.2 | 2.18 | 2.23 | 7.26 | 5.11 | | |
| v | 68.9 | 16.8 | 13.8 | 24.2 | 167 | 3.10 | 2.13 | 17.5 | 7.94 | | |
| Cr | 2.85 | 0.60 | 25.4 | 2.23 | 40.9 | 0.98 | bdl | bdl | bdl | | |
| Co | 1.08 | 1.02 | 0.88 | 0.96 | 1.24 | 4.15 | 0.70 | 0.98 | 0.86 | | |
| Ni | 0.90 | 0.78 | 0.70 | 0.79 | 1.18 | 1.88 | 0.34 | 0.40 | 0.82 | | |
| Cu | 0.86 | 3.37 | 1.08 | 2.23 | 1.47 | 1.73 | 1.15 | 0.10 | 0.13 | | |
| Zn | 24.3 | 24.1 | 24.2 | 26.3 | 29.4 | 98.8 | 21.0 | 33.5 | 30.3 | | |
| Ga | 86.1 | 78.9 | 82.0 | 81.0 | 98.7 | 66.7 | 76.5 | 66.6 | 66.7 | | |
| Rb | 708 | 652 | 717 | 717 | 664 | 666 | 512 | 628 | 594 | | |
| Sr | 6.58 | 7.53 | 7.11 | 7.10 | 3.93 | 6.01 | 8.66 | 5.72 | 6.27 | | |
| Y | 0.35 | 0.35 | 0.22 | 0.16 | 0.87 | 0.17 | 0.41 | bdl | 0.02 | | |
| Zr | 11.9 | 12.7 | 7.69 | 6.45 | 6.10 | 5.30 | 12.5 | 0.81 | 0.51 | | |
| Nb | 77.5 | 31.6 | 29.9 | 29.2 | 70.2 | 4.59 | 1.59 | 12.8 | 6.40 | | |
| Ва | 422 | 442 | 569 | 671 | 241 | 367 | 603 | 688 | 755 | | |
| Hf | 0.18 | 0.05 | bdl | 0.24 | 0.37 | 0.02 | bdl | 0.07 | 0.01 | | |
| Та | 15.5 | 3.66 | 4.41 | 4.16 | 11.2 | 0.27 | 0.07 | 1.23 | 0.42 | | |
| Tl | 3.54 | 2.98 | 3.53 | 3.75 | 2.79 | 4.31 | 2.68 | 2.58 | 2.38 | | |
| Pb | 3.74 | 4.06 | 3.35 | 3.75 | 2.84 | 3.54 | 4.33 | 2.32 | 2.14 | | |
| Th | 0.14 | 0.14 | 0.08 | 0.05 | 0.03 | 0.06 | 0.15 | bdl | bdl | | |
| U | 0.21 | 0.23 | 0.10 | 0.11 | 0.31 | 0.22 | 0.21 | 0.02 | bdl | | |
| REE (ppm) | | | | | | | | | | | |
| La | 0.58 | 0.07 | bdl | 0.15 | 0.22 | bdl | bdl | bdl | bdl | | |
| Ce | 0.68 | 0.19 | bdl | 0.30 | 0.22 | bdl | bdl | bdl | bdl | | |
| Pr | 0.86 | 0.13 | bdl | 0.04 | bdl | bdl | bdl | bdl | bdl | | |
| Nd | 0.29 | 0.05 | bdl | 0.18 | bdl | 0.05 | 0.22 | bdl | bdl | | |
| Sm | 0.38 | 0.08 | 0.03 | 0.05 | bdl | bdl | bdl | bdl | bdl | | |
| Eu | 1.87 | 0.42 | 0.03 | 0.05 | bdl | bdl | bdl | bdl | bdl | | |
| Gd | 0.06 | 0.07 | bdl | 0.02 | bdl | bdl | bdl | bdl | bdl | | |
| Tb | 0.01 | 0.08 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | | |
| Dy | 0.16 | 0.04 | bdl | 0.02 | bdl | bdl | bdl | bdl | bdl | | |
| Но | 0.22 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | | |
| Er | 0.49 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | | |
| Tm | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | | |
| Yb | 0.02 | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | | |
| Lu | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | bdl | | |

Abbreviations mineral after Kretz (1983). Muscovite 1 and 2 correspond to different analyzed mineral grains

bdl below detection limit

andalusite (P', Fig. 7), better allows for andalusite crystallization prior to primary muscovite formation (field A'; Fig. 7). Moreover, the field for potentially magmatic andalusite is even larger and probably more realistic, if the Richardson et al. (1969) andalusite–sillimanite equilibrium curve is considered (Fig. 7; curve R69).

| Table 9 Geothermobarometry for the La Costa plutor | Table 9 | Geothermobarometry | for the | e La | Costa r | oluton |
|--|---------|--------------------|---------|------|---------|--------|
|--|---------|--------------------|---------|------|---------|--------|

| Calibration method | Mineral assemblage / | P, T values | |
|--|------------------------|------------------|------------------------|
| | Zr concentration (ppm) | <i>T</i> (°C) | <i>P</i> (kbar) (±0.1) |
| Anillaco igneous facies, sample ANI-03 | | | |
| Ganguly and Saxena (1984) | Grt-Bt | 733 ^a | |
| Hoisch (1990) R2 model | Grt-Bt-Pl-Qtz | | 1.9 |
| Hoisch (1990) R4 model | Grt-Bt-Ms-Pl-Qtz | | 1.8 |
| Santa Cruz igneous facies | | | |
| Zircon saturation temperature $(T_{\rm Zr})^{\rm b}$ | 99 ^c | 758 | |

Composition of the Anillaco facies garnet (analysis number 14-15-16-21-22-23), biotite (45-46-47-48), muscovite (37-38-39-40-49) and plagioclase (29-30-31-33) in the calculations are mean values from Alasino (2007)

^a See uncertainty discussion in Ganguly and Saxena (1984) and Anderson (1996)

^b T_{Zr} =12,900/[2.95 + 0.85M + ln(476,000/Zr_{melt})], where $D^{Zr,zircon/melt}$ = (476,000/Zr_{melt}) is the ratio of Zr concentration (ppm) in zircon to that in the saturated melt; M is a compositional factor that accounts for dependence of zircon solubility on SiO₂ content and peraluminosity of the melt [(Na + K + 2Ca)/Al × Si), all values as cation fractions] (Watson and Harrison 1983 with rearranging after Miller et al. 2003)

^c Zirconium concentration in the Santa Cruz igneous facies from the average of Table 2

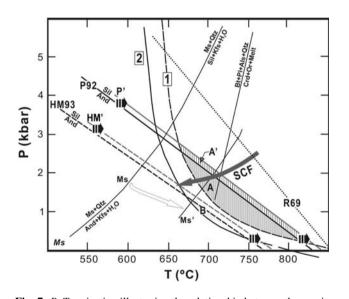


Fig. 7 P-T projection illustrating the relationship between the granite solidus, the And-Sill boundary and the Ms + Qtz stability field. SCF hypothetical Santa Cruz igneous facies P-T path. A Field for Al-silicate crystallization prior to primary Ms crystallization, bounded by the wet granite solidus and the And-Sill equilibrium curve P92. A' the And + melt field is bounded by the wet granite solidus and the And-Still equilibrium curve P'. B the And + melt field is bounded by the Al₂O₃-saturated granite solidus and the And-Still equilibrium curve HM'. 1 Wet granite solidus (Johannes and Holtz 1996), 2 Al₂O₃saturated granite solidus (Johannes and Holtz 1996), R69 Richardson et al. (1969), P92 And-Still boundary (Pattison 1992), HM93 And-Still boundary (Holdaway and Mukhopadhyay 1993). HM' and P' Shifting of the And-Still boundary (Holdaway and Mukhopadhyay 1993 and Pattison 1992, repectively) due to the Fe³⁺ content of andalusite (see text). Ms' empirical equilibrium curve for the reaction: $Ms + Qtz = Kfs + Al-silicates + H_2O/Melt$ (D'Amico et al. 1981). Experimental curves for the reaction Ms + Qtz = Kfs + Al-silicates $+ H_2O/Melt$ and Bt + Pl + Al-silicates + Qtz = Crd + QtzOr + Melt are from Pattison and Tracy (1991)

Cordierite

Textural evidence, along with whole-rock and mineral chemical compositions, suggests that Na- and Li-rich cordierite of the Santa Cruz igneous facies crystallized from a peraluminous magma, and that it was at some stage in equilibrium with andalusite (see also Clarke 1995; Erdmann et al. 2004; Clarke et al. 2005; Dahlquist et al. 2005). The chemical composition of the Na- and Li-rich cordierite is consistent with the whole-rock chemistry of the Santa Cruz monzogranite. This granitoid has SiO₂ content (65.3-68.6 wt%; Table 2) remarkably lower than other two other granitic facies of the La Costa pluton (ca. 74 wt%; Alasino et al. 2006). However, the contents of alkalis and other incompatible elements such as Li, Be, Rb and Cs in the Santa Cruz monzogranite are high relative to its silica content (Table 2). It seems that melt composition is the most important single factor controlling mineral/melt partition coefficients. The best constraints on mineral/melt partition coefficients in a low-pressure peraluminous anatectic system are those of Bea et al. (1994), who estimate crystal/melt partition coefficients as the concentration ratios between peraluminous leucosomes (interpreted as pure melts) and mesosome minerals, using a laser probe coupled to an ICP mass spectrometer. These authors demonstrate that cordierite crystallizing in peraluminous magmas strongly fractionates Li, Be, Rb and Cs, and is thus an efficient crystalline reservoir for these elements in magmas strongly enriched in aluminium, at crystallization temperatures of $\sim 750^{\circ}$ C, similar that observed for the Santa Cruz igneous facies.

Conclusions

- The Santa Cruz igneous facies of the La Costa pluton is an S-type granitoid with andalusite, Na- and Li-rich cordierite and primary muscovite. Petrography, mineral chemistry and whole-rock chemistry support magmatic crystallization for all three minerals. Secondary low-T muscovite formed under subsolidus conditions, largely after andalusite and Na- and Li-rich cordierite.
- 2. The Santa Cruz igneous facies crystallized at a moderate depth (ca. 1.9 kbar). At this pressure, crystallization of primary muscovite was favored by both depression of the granite solidus due to Al saturation, and the fluxing effect of B, Li and P in the magma. Moreover, the stability field of muscovite (+quartz) was probably significantly increased relative to the experimental one. Andalusite crystallization from the magma at pressure of ca. 2 kbar implies that the more realistic And-Sill boundary should be that of Pattison (1992) or that of Richardson et al. (1969). Upward shifting by ca. 13°C of the boundary due to Fe³⁺ content in andalusite also contributed to expansion of the andalusite stability field.
- 3. High Na and Li contents in cordierite are reported for the first time from a relatively low-silica monzogranite. Magma composition was relatively rich in incompatible elements, leading to crystallization of Na-rich cordierite markedly enriched in Li (654–3,043 ppm) and Be (82–1,879 ppm); the micas also show enrichment in some trace elements, such as Rb, Li, Cs, Ba, Nb, Zn, V, P and Sc. Contents of trace elements in andalusite are low except for P, V, Li and Ga.
- 4. Substitution in the unusual Na- and Li-rich cordierites was of the type: $^{Ch}Na^+ + ^{VI}Li^+ = {}^{Ch}[] + {}^{VI}Mg^{2+}$, leading to almost complete occupancy of the octahedral sites.

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