Maturing Arc Signatures Monitored by Trace Element and Hf Isotope Systematics in the Early Cretaceous Zacatecas Volcanic Field, Mexico

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ABSTRACT

Mesozoic growth of continental crust along the southwestern margin of North America and its southern extension in Mexico has been partly explained by the accretion of terranes. These terranes have been considered to be fragments of exotic, intraoceanic island arcs that approached mainland Mexico after the Early Cretaceous. Trace elements and Lu-Hf isotopic systematics for primitive arc successions of the Zacatecas Volcanic Field indicate a close relationship with parts of the northern Guerrero superterrane. Major and trace element systematics of lava flows and dioritic rocks from laccoliths suggest a cogenetic origin of the Zacatecas Formation and Las Pilas Complex rocks, here combined in the Zacatecas Group. This group represents a single arc succession that evolves from a primitive to mature arc. Initial $^{176}\text{Hf}/^{177}\text{Hf}$ (age corrected to 130 Ma) ranges from 0.28296 to 0.28307, corresponding to $\epsilon\text{Hf}(t) = +9.3$ to $+13.4$, indicating a source related to a depleted mantle wedge with a superimposed subducted sediment contribution. Based on combined field and geochemical evidence, we propose an arc model and suggest a spatial extension of paleoarc spreading north–south from Baja California beyond the present-day Trans-Mexican Volcanic Belt in the Early Cretaceous.

Online enhancements: supplementary tables.

Introduction

The study of modern island arc systems can help to reconstruct paleotectonic environments and, with this, contribute to a better understanding of modes of formation, growth, and evolution of active continental margins. Studies of intraoceanic arc systems show that subduction zones evolve from infant stages shortly after subduction initiation toward mature arc systems [e.g., Hergt and Woodhead 2007]. This transition is best reflected in the geochemical nature of the mantle wedge by an ultradepletion history and long-term overprint by slab-derived fluids [Tatsumi et al. 1992; Miller et al. 1994; Pearce and Peate 1995; Hergt and Woodhead 2007; Escuder-Viruete et al. 2009]. In maturing arcs, the geochemistry of both island arc basalts (IAB) and associated sediments show increasing crustal influence deviant from a mid-ocean ridge basalt (MORB) source. However, complications may arise from crustal assimilation superimposed on source characteristics so that geochemical tracing of arc sources is not straightforward. In addition, accreted arc systems have often been subject to low or intermediate metamorphic overprints, which may promote some geochemical changes and obliterate the original chemical signatures.

In this contribution, we study the major and trace element geochemistry and Hf isotope composition of a series of basaltic rocks and sediments from an accreted terrane in central Mexico that are inter-
Figure 1. a, Map of Mexico showing study area and location of the Guerrero superterrane [boldface dashed line] and subterranes [names in italics; modified from Campa and Coney 1983; Dickinson and Lawton 2001; Centeno-García et al. 2008]. The Sierra Madre Occidental is based on Ferrari et al. (2005). The underlined names are from massive sulfides. The $\varepsilon_{Nd}(t)$ values were taken from Verma (1984, 1993), Schaaf (1990), Böhnel et al. (1992), Lapierre et al. (1992), Centeno-García et al. (1993), Tardy et al. (1994), Schaaf et al. (1995), Centeno-García and Silva-Romo (1997), Freydier et al. (1997, 2000), and Valdez-Moreno et al. (2006). The $\varepsilon_{Nd}(t)$ contour values were performed following the nearest neighbor procedure. Values of $\varepsilon_{Nd}(t) < +2.0$ were not plotted because they merge with the zero values where there are no available data. b, Simplified geologic map of the study area [modified from Escalona-Alcázar et al. 2009] showing the location of the samples for geochemistry and Hf isotopic analysis. Cities are in boldface, subterranes are in italics, and massive sulfides are underlined.

Regional Geology

The Guerrero superterrane is exposed at the southeastern and southern ends of the Sierra Madre Occidental and divided into northern and southern successions by the Trans-Mexican Volcanic Belt (TMVB; fig. 1). Its location and mafic nature have been key in studying the accretionary history of
western Mexico, leading to the development of a fringing arc model for its northern (Busby et al. 1998; Busby 2004) and southern exposures (Centeno-García et al. 2011). The Guerrero superterrane is considered an association of island-arc, back-arc, and ocean-floor assemblages of Late Jurassic–Early Cretaceous age (Campa and Coney 1983; Centeno-García et al. 1993). However, its paleolocation and relationship with mainland Mexico, either as an exotic terrane or as an island arc, is still a matter of debate (Campa and Coney 1983; Lapiere et al. 1992; Sedlock et al. 1993; Dickinson and Lawton 2001; Centeno-García et al. 2008; Mortensen et al. 2008; Martini et al. 2013). Traditionally, the assemblage of arcs in various terranes in the southwest United States and in Mexico were described as exotic terranes representing outboard arcs that were accreted to the continental margin of North America (Campa and Coney 1983; Centeno-García et al. 1993; Sedlock et al. 1993; Dickinson and Lawton 2001; Umhoefer 2003; Talavera-Mendoza et al. 2007). A fringing arc evolution as an alternative explanation for the juxtaposition of terranes has been proposed for the northwestern part of the superterrane, i.e., in the Alisitos subterrane of the Baja California peninsula (fig. 1a; Busby et al. 1998; Busby 2004). In this model, a Triassic-Jurassic island arc was separated from the continent by a possibly narrow back-arc basin. During subsequent arc evolution, this basin suffered an extensional phase, followed by converging forces, prior to accretion to mainland Mexico (Busby et al. 1998; Busby 2004; Alsleben et al. 2008). Whereas this explanation seems most plausible for the Baja California succession, the evolution of its southern extension is yet to be established. If this is indeed the case, the fringing arc model envisages fundamental processes to explain the growth of the continental crust at the margin of the southwestern Cordillera.

South of the TMVB, the tectonic setting and petrogenetic models of the Guerrero superterrane have been defined mostly on the basis of field data, supported by some trace element abundances and $^{147}$Sm,$^{144}$Nd, $^{87}$Rb-$^{87}$Sr, and, to a lesser extent, $^{207}$Pb-$^{206}$Pb isotope systematics. Based on these data, up to three independent island arcs have been proposed: Zihuatanejo, Teloloapan, and Arcelia (fig. 1a; Lapiere et al. 1992; Centeno-García et al. 1993, 2003, 2011; Tardy et al. 1994; Freydier et al. 2000; Talavera-Mendoza et al. 2007; Martini et al. 2009, 2010; Vega-Granillo et al. 2012). In particular, MORB-like Nd isotope signatures, i.e., $e_{\text{Nd}}(t) > +8$, in lithologic units from central Mexico have been used to favor an exotic terrane assemblage, likely representing an intraoceanic arc system (Lapiere et al. 1992). Moreover, isotope systematics (Rb-Sr and Sm-Nd) of Late Cretaceous plutons exposed along the southwest Mexican continental margin (e.g., Puerto Vallarta, Manzanillo, Jilotlán) record the southeast waning of arc magmatism, evidenced by increasing crustal assimilation (Verma and Luhr 1993; Valdez-Moreno et al. 2006; isotope data from Schaaf 1990 were published in Böhnel et al. 1992, Schaaf et al. 1995).

The eastern and northern edges of the Guerrero superterrane included ocean floor–like assemblages (Lapiere et al. 1992; Tardy et al. 1994; Freydier et al. 1997) and ultramafic associations. Ultramafic rocks at the southwestern edge of the superterrane are probably ocean-floor related (Ortega-Gutiérrez et al. 1979), whereas those in the southeast are arc related (Delgado-Argote et al. 1992). North of the TMVB, the Guerrero superterrane is widely covered by Tertiary volcanic rocks of the Sierra Madre Occidental. The documented outcrops in Guanajuato (fig. 1a) were interpreted as nascent intraoceanic arc and oceanic crust (Lapiere et al. 1992; Ortiz-Hernández et al. 1992, 2003; Tardy et al. 1992, 1994). Further to the northwest, a possible back-arc setting developed in San Nicolás (Mortensen et al. 2008) and Francisco I. Madero (Yta et al. 2003), both of which are located in the state of Zacatecas (fig. 1a).

Based on field relationships, Centeno-García et al. (2011) suggested that the southwesternmost arc, the Zihuatanejo subterrane, possibly evolved as a fringing arc, placing the Guerrero superterrane close to the continental margin. Such interpretation implies that the fringing arc model proposed for the Baja California peninsula (Busby et al. 1998; Busby 2004) could be extended southward as far as the Sierra de Zacatecas (Escalona-Alcázar et al. 2009) and Guanajuato (Lapiere et al. 1992; Tardy et al. 1992; Freydier et al. 1996).

**Geology of the Zacatecas Group.** The study area is located in the state of Zacatecas, Mexico (fig. 1). Several investigations on the Sierra de Zacatecas have suggested two main Mesozoic lithologic units in tectonic contact: the lower Zacatecas Formation and the upper Las Pilas Complex (Ponce and Clark 1988; Monod and Calvet 1992; Centeno-García et al. 1993; Centeno-García and Silva-Romo 1997; Bartolini et al. 2001). Recently, Escalona-Alcázar et al. (2009) identified these two units as one continuous sequence that formed in the Early Cretaceous. The older unit is the dominantly sedimentary Zacatecas Formation (ZF) that grades to the younger, dominantly volcanic Las Pilas Complex (LPC).
Contact relationships between the ZF and LPC units are gradual. The ZF is composed of feldspathic wacke, mudstone, chert, and discrete limestone lenses, accompanied by basaltic lava flows, rare dikes, and hydrothermal vent–like structures. The LPC is mainly composed of laccolithic intrusions and basaltic lava flows, interlayered with feldspathic and lithic wacke, mudstone, chert, and rare limestone. This assemblage is here referred to as the Zacatecas Group.

Available geochemical data for the Zacatecas Group are limited. Because these rocks underwent hydrothermal/deuteric alteration and greenschist facies metamorphism, fluid-mobile elements such as K, Na, Rb, or Sr need to be treated with caution in petrogenetic and tectonic interpretation. In the Zacatecas Formation, limited Sm-Nd isotopic studies on three samples indicate a primitive igneous suite, interpreted to be akin to ocean-floor assemblages (Centeno-García and Silva-Romo 1997). For the Las Pilas Complex, Ranson et al. [1982] presented major elements and two trace elements (Rb and Sr) for five igneous rocks. However, due to hydrothermal/deuteric alteration, these results may be compromised by secondary processes rather than reflect primary igneous signatures. Verma [1984] analyzed Rb-Sr and Sm-Nd isotopes in one basaltic sample from the LPC and inferred that oceanic crust was involved in its magma generation. Subsequently, Tardy et al. [1992, 1994] and Centeno-García and Silva-Romo [1997], based on two igneous rock samples, defined an island arc tectonic setting. It is noteworthy that only Verma [1984] mentioned the sample location; all the other samples are from unknown localities. In summary, all previous analyses suggest a primitive, mantle-derived origin for the volcanic rocks but with opposing tectonic interpretations [IAB vs. MORB] and based on rather limited data. Hence, our systematic approach of sampling volcanic, plutonic, and sedimentary rocks in conjunction with the robustness—i.e., dominantly fluid immobile nature—of the Lu-Hf isotope system during alteration offers a promising way to reevaluate the tectonic framework of this terrane.

**Analytical Procedure**

Fifteen samples comprising six plutonic and nine volcanic rocks were collected from the Mesozoic sequence of the Sierra de Zacatecas for geochemical analyses [table S1; tables S1–S3 are available online]. Of these, four volcanic and five plutonic rock samples, along with four sedimentary rock samples, were analyzed for Lu-Hf isotope systematics. Coarse rock samples were processed for geochemical analyses in the facilities of the Department of Geology, Centro de Investigación Científica y Educación Superior de Ensenada. Approximately 1 kg of each sample was crushed using a jaw crusher and subsequently powdered in a tungsten carbide mill. Major and trace element analyses were performed in the ActLabs Laboratories, Canada, on fused lithium tetraborate discs [1 : 4 dilution]. Rock powders were mixed with internal standards prior to the melting procedures, and fusion discs were subsequently digested in nitric acid. Major elements were measured with an ENVIRO II ICP-OES [Thermo Jarrell], and trace elements were analyzed with a SCIEX ELAN 600 ICP-MS [Perkin-Elmer]. Data quality was monitored with an in-house standard (sample 34/XII/05) that was cross-calibrated against standard reference materials, and obtained results are within previous results for the same sample. The geochemical analyses are listed in table S1.

Taking into account the hydrothermal alteration, we employed immobile elements Y, Zr, Ti, and Nb for classification and petrogenetic interpretation (Winchester and Floyd 1977; MacLean and Barret 1993). The normalizing values of rare earth elements [REEs] and MORB [N-MORB] are taken from Sun and McDonough [1989].

For Lu-Hf isotopic analyses, samples were powdered in an agate mortar to avoid contamination from tungsten carbide. Approximately 100 mg of each sample was spiked with a $^{176}$Lu-$^{176}$Hf isotope tracer and dissolved in 3-mL Savillex teflon vials in high-pressure autoclaves [bombs] in an acid solution of $\sim 1 : 1$ HF : $\text{HNO}_3$. Once evaporated, the samples were dried three times with 2 mL of $\text{HNO}_3$ and traces of HF (<0.05 M) and then equilibrated with 6 M HCl. The Lu-Hf separation from the rock matrix and details of the isotope tracer are listed in Morel et al. [2008].

Isotope measurements were performed on an MCICPMS Thermo Fisher Neptune at Vrije Universiteit Amsterdam, The Netherlands, following the protocol listed in Nebel et al. [2009]. The JMC-475 Hf isotope standard gave a mean of $^{176}$Hf/$^{177}$Hf = 0.282159 ± 8, and all samples were corrected relative to a value of 0.282160 for international data comparison. Procedural blanks of 10 pg and 25 pg for Lu and Hf, respectively, were in the range of the long-term laboratory blanks [Nebel et al. 2009] and negligible.

**Results**

**Petrography.** The lava flows of the Zacatecas Formation have porphyritic textures with plagioclase...
Figure 2. a, Classification diagrams for altered igneous extrusive rocks (Pearce 1996). b, Diagram showing the calc-alkaline, transitional, and tholeiitic affinities (MacLean and Barret 1993). c, Modal classification of the intrusive bodies from Las Pilas Complex (after Le Maitre 2002).
subalkaline [fig. 2a]. The tholeiitic nature and magmatic differentiation can also be seen in figure 2b, where rocks with higher Zr/TiO₂ plot in the transitional field.

The magmatic differentiation was further evaluated by using Mg# versus FeO⁺ (fig. 3a) and Al₂O₃ versus Mg# (fig. 3b). In terms of Mg#, the volcanic rocks from the Zacatecas Formation plot on the tholeiitic trend, with a slight increase in FeO⁺ as the Mg# decreases. Las Pilas Complex samples tend to cluster in the edge between the tholeiitic and calc-alkaline trends (fig. 3a, 3b). The plutonic rocks have a tendency toward the calc-alkaline trend (fig. 3a, 3b). The Al₂O₃ increases as the Mg# decreases (fig. 3b); this is related to the delay in plagioclase fractionation, as is typical for tholeiitic series. Crystal fractionation was further evaluated by using distributions of selected trace elements indicative for key phases, i.e., Ni for olivine and Sr for plagioclase. For this purpose, samples from lava flows are placed in their stratigraphic order (fig. 3c). Figure 3c shows that upward in the stratigraphic section, Ni has a slight negative slope, indicative for a decrease in olivine, whereas the Sr slope is positive, indicating plagioclase fractionation.

The tholeiitic character of the sequence is also observed in figure 3d in [Ba/La]₃ versus [La/Sm]₃ (Arculus and Powell 1986). In this diagram, the island arc affinity of the sequence is confirmed by an increase in [Ba/La]₃ reflecting alkali enrichment by slab-derived fluids (Arculus and Powell 1986; Woodhead et al. 2001).

**Rare Earth Element and Multielement Patterns.** The two lava flows of the Zacatecas Formation (fig. 4a) show almost flat REE patterns with slightly depleted light rare earth elements ([La/Sm]₃ = 0.8–0.94) and positive Eu/Eu⁺ anomalies (1.15–1.24). The REE patterns with 20–30 times chondrite values are in the range of other island arc basalts (Wilson 1989), which is likely caused by crystal fractionation. Such fractionation is more evident from the patterns of the volcanic and plutonic rocks.
of the Las Pilas Complex, where total concentration increases and LREE exhibit an increment with respect to chondrite 10–40 times in volcanic rocks and 20–60 times in the laccolithic bodies (fig. 4a, 4b). The slight increase in LREE and the persistent positive Eu anomaly in the two sequences correlate with the enrichment in incompatible elements (Gill 2010).

The positive Eu/Eu* anomaly suggests plagioclase accumulation, and the flat to fractionated trend for the middle rare earth elements and heavy rare earth element (HREEs) indicates neither residual garnet during melting nor the presence of refractory minerals such as monazite, rutile, or sphene.

In the normalized trace element diagrams of the volcanic rocks from the Zacatecas Group, the volcanic and plutonic rocks show similar patterns (fig. 5). There is a slight negative anomaly in Nb, as is typical for IAB. The Zr and Ti have small positive spikes, whereas the Sr is more enriched. These values are typical from ocean island arc tholeiitic basalts, with melts derived from a depleted mantle that is becoming enriched by adding fluids from the subducted slab (Wilson 1989). The similarity in the patterns shown in figure 5 confirms a comagmatic origin of the entire Zacatecas Group.

**Lu-Hf Isotope Systematics.** The Lu and Hf isotope results, as well as initial Hf isotope compositions corrected to an assumed age of 130 Ma and TDM_{Hf} model ages of the igneous and sediments suites, are listed in table S3. The 176Hf/177Hf ratios range from 0.28302 to 0.28314 for basalts, from 0.28299 to 0.28305 for diorites, and from 0.28276 to 0.28297 for sediments. The Lu/Hf ratios of all volcanic rocks of the Zacatecas Group are in the range of global island arc rocks (Vervoort and Blichet-Toft 1999). One basalt sample (70) has a 176Lu/177Hf of 0.0538 that exceeds by far those of the average depleted mantle of 176Lu/177Hf = 0.03836 (Weber et al. 2012), indicating a cumulus effect. A similar but minor effect is also observed in basalt sample 79, which has a 176Lu/177Hf of 0.0340, close to the depleted MORB mantle (DMM), yielding an overestimated TDM_{Hf} of 1091 Ma (table S3). The eHf_{130Ma}
values range from +10.2 to +13.4 in basalts and from +9.3 to +11.4 in diorites, all of which are clearly below the DMM composition of $\varepsilon$Hf$_{[130\text{Ma}]} \approx +17.5$. Sedimentary rocks yield $\varepsilon$Hf$_{[130\text{Ma}]}$ values between +1.5 and +8.6, suggesting crustal sources admixed to a dominantly arc-derived detritus (cf. Vervoort and Blichert-Toft 1999) that is also reflected in TDM$_{[130]}$ from 931 to 579 Ma.

**Discussion**

**An Arc Origin of the Zacatecas Group.** To evaluate the nature of the mantle source of the primitive igneous rocks and to test if the samples are indeed arc related, we use ratios of elements with different compatibility during melting and different affinities during slab fluid transport. A comparison with global MORB (Jenner et al. 2012), the Aleutian arc (a fluid-dominated arc setting), and the present-day TMVB (which is dominated by evolved crustal compositions data taken from the georoc database, http://georoc.mpchmainz.gwdg.de/georoc) is used to investigate the geochemical setting, which formed the Zacatecas Group.

Ratios of immobile elements usually reflect the contribution from the subducted slab (Pearce and Peate 1995), either in the form of sediment melts or a fluid component with elevated Th/Yb. Likewise, in fluid-dominated arcs, the Nb/Yb indicates the source fertility with exhaustion of Nb over Yb in maturing arcs. Hence, in an island arc, setting the Yb-normalized ratios of Th-Nb is an effective way to distinguish between arc settings deviant from the MORB array and paleo-ridge segments (Pearce and Peate 1995). In figure 6, it is demonstrated that Zacatecas samples clearly plot off the MORB array, indicating an island arc setting.

The La/Nb ratio support this view, with values ranging from 1.4 to 2.8, which are elevated compared to MORB (Rollinson 1993). These variations possibly reflect a subducted slab component. Zirconium is an HFSE and considered immobile in arc fluids (e.g., Woodhead et al. 2001). When normalized to Yb, Zr can reflect enrichment of the mantle source in trace elements by sediment melts or indicate the crustal character of arc rocks. In figure 6a, we show that all samples of the Zacatecas Group overlap with samples from the Aleutian arc, which is an intraoceanic arc dominated by slab fluids. However, some samples of the Las Pilas Complex laccoliths tend toward more evolved compositions and approach compositions of the present-day TMVB. These chemical features, together with field evidence, indicate a younging succession from the lower and older Zacatecas Formation toward the overlying, younger Las Pilas Complex and suggest that the arc suite evolves from primitive to mature and/or more crustal compositions.

Escalona-Alcázar et al. (2009) argued that the Zacatecas Group is composed of two conformable units. These two units exhibit two trends with depletion and enrichment in LREE. Based on a limited

**Figure 6.** Comparison of immobile elements ratios from the Zacatecas Group with present-day tectonic settings: mid-ocean ridge basalt (MORB; Jenner et al. 2012), the Aleutians, and the Trans-Mexican Volcanic Belt (TMVB, both from the georoc database, http://georoc.mpchmainz.gwdg.de/georoc/). Abbreviations, in alphabetic order: LPC-E = Las Pilas Complex lava flows, LPC-I = Las Pilas Complex laccolithic bodies, ZF = Zacatecas Formation. The Zacatecas Group tends from a MORB source toward the present-day TMVB, indicating increasing island arc signatures.
number of samples, Centeno-García and Silva-Romo [1997] obtained depleted LREE patterns from two volcanic samples of the older Zacatecas Formation, which were interpreted in terms of an ocean-floor association. Opposing this view, in the younger Las Pilas Complex, Tardy et al. [1992, 1994] obtained enriched LREE patterns in two samples and proposed an island arc setting. The same contrasting results were also used as argument to support the existence of two distinct stratigraphic units. By using our systematic sampling approach for the Sierra de Zacatecas and considering that the stratigraphic sequence appears continuous, our sequential sampling shows an almost flat REE pattern. Abundances in the Zacatecas Formation are almost twice as enriched compared to the lower part of the Las Pilas Complex. The LREEs in the Las Pilas Complex show a gradual increase from the bottom to the top of the complex [fig. 7a]. These evolving patterns obtained in both units not only support a cogenetic relationship but also likely reflect the evolution of the island arc tholeiite as the arc becomes mature.

The REE patterns obtained for other island arc subterranes of the Guerrero superterrane also support this interpretation. In particular, the intrusive rocks of the Las Pilas Complex overlap with patterns of the Tuna Mansa Diorite and the Santa Ana Dike Complex, located about 200 km southeast within the Guanajuato region, with the exception of the low LREE observed in the Guanajuato units [figs. 1, 7b; Ortiz-Hernández et al. 1992]. The Early Cretaceous magmatic sequence in Guanajuato has been interpreted as having a common magmatic origin [Ortiz-Hernández et al. 1992; Tardy et al. 1992, 1994; Mendoza and Suastegui 2000].

In addition to LREE enrichment, the spider diagrams of the igneous rocks of the Zacatecas Group show negative Nb anomalies that are a typical feature of many island arcs [fig. 5; Wilson 1989; Miller et al. 1994; Clift and Lee 1998; Falloon et al. 2007; Hergt and Woodhead 2007], including those of the genetically akin Guerrero superterrane.

In summary, the geochemical arguments, together with field relationships, reinforce the hypothesis that the Zacatecas Group and the Las Pilas Complex form a group that developed in an arc environment, notably geochemically similar to other subterranes of the Guerrero superterrane.

We thus conclude that the Zacatecas Group is the remnant of an arc sequence that was fluid dominated, possibly growing in crustal components in a maturing arc.

**Constraints from Hf Isotope Compositions.** The initial Hf isotope compositions of the igneous rocks are deviant from age-corrected DMM. This indicates a crustal component in the rocks, which in island arc settings can be due to contribution of sediments from the subducted slab [fig. 8a; Pearce et al. 1999; Yogodzinski 2010; Nebel et al. 2011].

The igneous rocks of the study area carry an εHf(t) signal that is intermediate between the mantle wedge source (assumed to be similar to DMM) and the sediments, with values ranging from +9.3 (diorite from the Las Pilas Complex) to +13.4 (basalt from the Zacatecas Formation). Hence, the ra-
diogenic Hf isotope composition is generally consistent with a source with time-integrated superchondritic Lu/Hf, i.e., a depleted mantle origin [fig. 8; Pearce et al. 1999]. Likewise, even though the magmas were presumably derived from a depleted mantle source, their model ages [listed in table S3] show a wide range that suggests the mixing of components with different residence times in different proportions. Given the above-mentioned constraints in an intraoceanic arc setting in the absence of evolved continental crust, such bias in the isotope composition is likely related to sediment contribution from the slab [Nebel et al. 2011].

In order to explore the contribution of sedimentary Hf, we compared our Hf isotope systematics with a modeled origin of positive/negative anomalies (expressed as Hf/Hf′) in an extended REE plot. The Hf/Hf′ represent the extrapolated space for Hf in REE compared to its actual position, and anomalies were calculated according to the Tollstrup and Gill [2005] model to define the crustal contribution in the magma generation. The model uses a mix of (i) a depleted mantle component and (ii) clay and volcanioclastic, the latter either with the dissolution of zircon [fig. 8b, line 1] or without a zircon contribution [fig. 8b, line 2], and assuming a maximum 25% melting [batch-melting model].

Igneous rocks from the Zacatecas Group plot close to the mixing line 1, which argues for a sediment melt. Notably, Hf/Hf′ have recently been attributed to crystal fractionation, in addition to source parameters of arc rocks [Handley et al. 2011; Woodhead et al. 2011]. All samples cluster around a value of Hf/Hf′ close to 1 [0.81–1.15], so that both source variability consequent to sediment melting and crystal fractionation may account for the observed effect. However, the covariations with isotope compositions argue for the former rather than the latter.

An intriguing fact is the correlation of 176Hf/177Hf of the igneous rocks with LREE [expressed as La/Sm, fig. 9]. Sediment melts show high [La/Sm]N, accompanied with low 176Hf/177Hf ratios and represent extension of the trend defined by igneous rocks. This indicates that local sediments are indeed possible end members for a mixing relationship. Assimilation of existing arc crust during magma ascent can have large effects on isotope and elemental abundances of new arc rocks, which, however, can be similar to effects caused by subducted continental material contribution to the magma source (Arculus and Powell 1986; McCulloch and Gamble 1991; Hawkesworth et al. 1993; Thirlwall et al. 1996; Woodhead et al. 1998). Crustal assimilation

Figure 8.  

| Figure 8. a, εHf(t) versus Hf/Yb fields taken from Pearce et al. [1999]. b, Hf/Hf′ anomalies versus εHf(t) mixing lines proposed by Tollstrup and Gill [2005] for the Marianas arc for depleted mantle with volcanioclastic sediments including marine clays with [1] and without [2] zircons. MORB = mid-ocean ridge basalt. |

Figure 9.  

| Figure 9. (La/Sm)N versus 176Hf/177Hf. Chondrite normalizing values from Sun and McDonough [1989]. |
and partial sediment melts from the top of the slab can be expected to result in distinct contamination paths in \([\text{La}/\text{Sm}]_\text{N}\) versus Hf isotopes (where subscript N denotes the normalization to chondritic abundances). Observed variations in \([\text{La}/\text{Sm}]_\text{N}\) in fluid-dominated shallow arc settings are minor \((0.3–3); e.g.,\) Pearce et al. 1999; Woodhead et al. 2001), including amphibole cumulates and rocks that experienced amphibole fractionation (Nebel et al. 2007). In contrast, deep island arc melts that have incorporated water-bearing-sediment-derived liquids show elevated \([\text{La}/\text{Sm}]_\text{N}\) of \(\geq 3\) [White and Dupré 1986; Thirlwall et al. 1996]. This is a consequence of higher liquid-solid residue partitioning LREE (e.g., La, Ce) over HREE (e.g., Yb, Lu) in hydrous melts or supercritical fluids from subducted sediment and the presence of residual HREE-retaining garnet (van Westrenen et al. 2001; Kessel et al. 2005; Rubatto and Hermann 2007; Klimm et al. 2008). The igneous rocks of the current study [fig. 9] show a trend of \(^{176}\text{Hf}/^{177}\text{Hf}\) from volcanic to plutonic rocks toward sediments, here interpreted to indicate a mixing of mafic magma with sedimentary melts.

Notably, this observation is consistent with previous suggestions of sedimentary contribution in the magma genesis of the greater Guerrero and Caribbean island arc chains (Tardy et al. 1992, 1994; Freydier et al. 1997; Kerr et al. 1999; Mendoza and Suastegui 2000; Centeno-García 2005; Marchesi et al. 2007; Centeno-García et al. 2011).

Our preferred scenario of sediment melt contribution can also explain the Nd isotope signatures in previous isotope studies: reported values for basalts from the Zacatecas Group range from \(e\text{Nd}(t) = +1.4\) to \(e\text{Nd}(t) = +7.2\) [Verma 1984; Centeno-García and Silva-Romo 1997], values that are in general agreement with those reported south of the TMVB, where \(e\text{Nd}(t)\) ranges from \(+1.6\) to \(+9.1\) [Freydier et al. 1997, 2000]. Whereas these values generally support a mantle origin for these rocks [Verma 1984; Centeno-García and Silva-Romo 1997], it seems obvious that their deviation from a pure DMM source requires slab fluids contribution, sediment melts, or crustal contamination. In light of our Hf isotope values and in conjunction with trace element constraints, sediment melts appear a feasible scenario for the Hf-Nd isotope compositions.

**The Guerrero Superterrane in a Fringing Arc Model.** Interpretations of the origin of the Zacatecas Group have considered two or three lithologic units of different age, each deposited or emplaced in different tectonic settings [Gutiérrez-Amador 1908; Monod and Calvet 1992; Centeno-García et al. 1993; Centeno-García and Silva-Romo 1997; Bartolini et al. 2001; Centeno-García 2005]. The oldest is the Zacatecas Formation, which has been interpreted to be deposited in an oceanic basin during the Late Triassic. The Nazas Formation of the Middle-Upper Jurassic is interpreted to be emplaced in a continental arc setting, whereas the youngest, the Las Pilas Complex, is interpreted as a Lower Cretaceous island arc. The Mesozoic tectonic evolution of western Mexico is related to an active continental margin developed in northern and western Mexico from the Permian to the Middle Jurassic [DeCserna et al. 1994; Barboza-Gudiño et al. 1998, 2008, 2010; Bartolini et al. 2001; Centeno-García et al. 2008]. The magmatism from the Late Jurassic to Early Cretaceous has been explained by two hypotheses: the first considers the arc magmatism to have been continuous in time but not space [Damon et al. 1981]. In this scenario, during the Late Jurassic, the active arc may have migrated toward the east, perhaps close to the actual west coast of Mexico [Lapierre et al. 1992; Tardy et al. 1992; Freydier et al. 1996; Barboza-Gudiño et al. 1998; Mendoza and Suastegui 2000; Umhoefer 2003; Talavera-Mendoza et al. 2007; Martini et al. 2010; Centeno-García et al. 2011]. In addition to this hypothesis, Martini et al. [2011] suggested a para-autochthonous arc model in which, initiated by slab rollback, the arc migrated to the west, where it formed an island arc that was separated from mainland Mexico by a back-arc basin [Arperos basin]. During the Late Cretaceous, the island arc accreted to the continent, thereby closing the Arperos basin [Martini et al. 2013]. The second hypothesis suggests that the arc developed simultaneously from the Late Jurassic to Early Cretaceous in two or three parallel island arcs. However, this model fails to explain necessary distances between the arcs and the continent [Mendoza and Suastegui, 2000; Dickinson and Lawton 2001; Talavera-Mendoza et al. 2007; Centeno-García et al. 2008; Escuder-Viruete et al. 2013]. However, Centeno-García et al. [2011], in a detailed study of the stratigraphy and U-Pb ages of detrital zircons of the Zihuatanejo subterrane, concluded that this subterrane evolved as an extensional arc. In such a model, the Zihuatanejo subterrane evolved as a fringing arc close to the continent, and the Zacatecas Formation is still considered an exotic block.

Our new interpretation of the igneous suites of the Zacatecas Group supports the first hypothesis for the tectonic evolution of central Mexico during the Mesozoic. Sampling of the Mesozoic sequence of the Sierra de Zacatecas reported in the current study indicates a magmatic affinity for the igneous units, even though they were probably generated.
at different stages during the evolution of the island arc. Hence, based on the field evidence and our geochemical interpretation, we argue for a single arc origin for all these units that evolved from a juvenile to a more mature stage.

We thus support an evolutionary scenario of a continuous arc rather than the existence of different arcs. In a paleotectonic context, the presence of continental crust has broader implications for the arc development. Our data support a fringing arc model similar to that described in the northern part of the Baja California peninsula (Busby et al. 1998, 2004), rather than an exotic arc model. Hafnium isotopes have been successfully applied to

Figure 10.  a, Paleogeographic model of the tectonic setting and evolution of the Zacatecas Group during the Hau-terivian. 1 = Pico de Teyra, 2 = Sierra de Catorce, 3 = Cañón de la Peregrina, 4 = Sierra de Salinas, 5 = Guanajuato, 6 = Arcelia, 7 = Huetamo, 8 = Oaxaca. The stippled pattern is oceanic crust. Modified from Pindell and Kennan (2009). b, A possible scenario of the development of the Zacatecas Group.
exotic outboard arcs, providing a true mantle signature, even in mature arc sequences (e.g., Nebel et al. 2007).

Our preferred model for the development of the Zacatecas Group in the Guerrero superterrane is illustrated in figure 10. In this model, the arc developed parallel and close to the continental margin (Busby et al. 2006; Alsleben et al. 2008; Martini et al. 2010, 2011; Centeno-Garcia et al. 2011), and Zacatecas is in the back side of the Alisitos-Teloloapan arc.

In our model, the Arperos basin possibly developed an oceanic-like crust in a back-arc basin behind the Guerrero arc, as earlier proposed (Tardy et al. 1994). In Zacatecas, ~10 km west of our study area, the Francisco I. Madero massive sulfide deposits possibly developed in an island arc setting as well (Yta et al. 2003). As the island arc evolves, the Las Pilas Complex was emplaced, forming a volcanic field in the W margin of the Arperos basin. The details of the distribution of the lithologic units are shown in figure 10b. This model is similar to that proposed by Escuder-Viruete et al. (2013) for the Caribbean arc and their extension in Mexico for the Guerrero superterrane. Our model further supports an arc development on oceanic-like crust covered by sediments of the Potosí fan along the western margin of Mexico. If there was a slab rollback, then the trench migrated to the west and the sediments could be subducted together with the oceanic Farallon plate (Martini et al. 2011). In this scenario, the mixing of sedimentary melt contribution with depleted mantle is the origin of the Hf isotope signatures for the magma generation.

We propose a fringing arc model for the evolution of central Mexico similar to that of the Guerrero superterrane at the western margin of North America. In this model, the island-arc, back-arc, and ocean-floor assemblages of the Late Jurassic–Early Cretaceous developed close to the continent, extending from the border of the United States with Mexico to south of the TMVB.

Conclusions

New Lu-Hf-isotope data from the Zacatecas Group coupled with trace element systematics indicate an island arc origin of the igneous rocks. On the basis of its geochemistry and age distributions, the island arc of the Guerrero superterrane represents different stages of the same arc section in various evolutionary stages. With respect to the continental hinterland of the outboard Guerrero arc, the Zacatecas-Teloloapan subterrane was likely in close proximity to a continent.

During magma genesis, a depleted mantle wedge experienced sedimentary melt contribution, resulting in the offset of isotope and trace elements from a pure DMM source. The sediment contribution may have been related to the proximity of the paleoarc to the North American continent. Hence, a fringing arc model that was first suggested for the Alisitos subterrane in Baja California can be extended south- and eastwards to the Zacatecas Group in Central Mexico. In this model, the arc could be separated from the continent by the Arperos basin, whose extension is unknown.

We thus conclude that the island arc of the Guerrero terrane shows a continuous evolution in time but with significant spatial variations that promoted the development of transitional arc crust in a maturing arc system.

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