# Geochemical window into subduction and accretion processes: Raspas metamorphic complex, Ecuador

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## ABSTRACT

**The high-pressure, low-temperature ($P$ = 1.3–2 GPa; $T \leq 600$ °C) Raspas metamorphic complex is an exhumed fragment of the partially accreted, partially subducted Amotape-Chaucha terrane in southwest Ecuador. Comparative analysis of major and trace elements plus Sr, Nd, and Pb isotopes in bulk lithologies and individual crystalline phases shows that the complex includes one to three layers of ordinary oceanic crust and underlying mantle lithosphere together with oceanic plateau fragments. Subduction (and exhumation) of oceanic lithosphere resulted in selective bulk trace element geochemical changes: Rb, Ba, and Sr have been lost (in amounts from approximately 85%–50%) from the high-$P$, low-$T$ metamorphosed pelites and basalts, whereas Pb is enriched in mafic rocks. During formation of the eclogite, U, Pb, and rare earth elements (REEs) were immobile. High-$P$, low-$T$ metamorphosed terranes form the basement of active Ecuadorian arc volcanoes; partial melting of this basement by mantle-wedge–derived basalt is a likely source of adakitic components.**

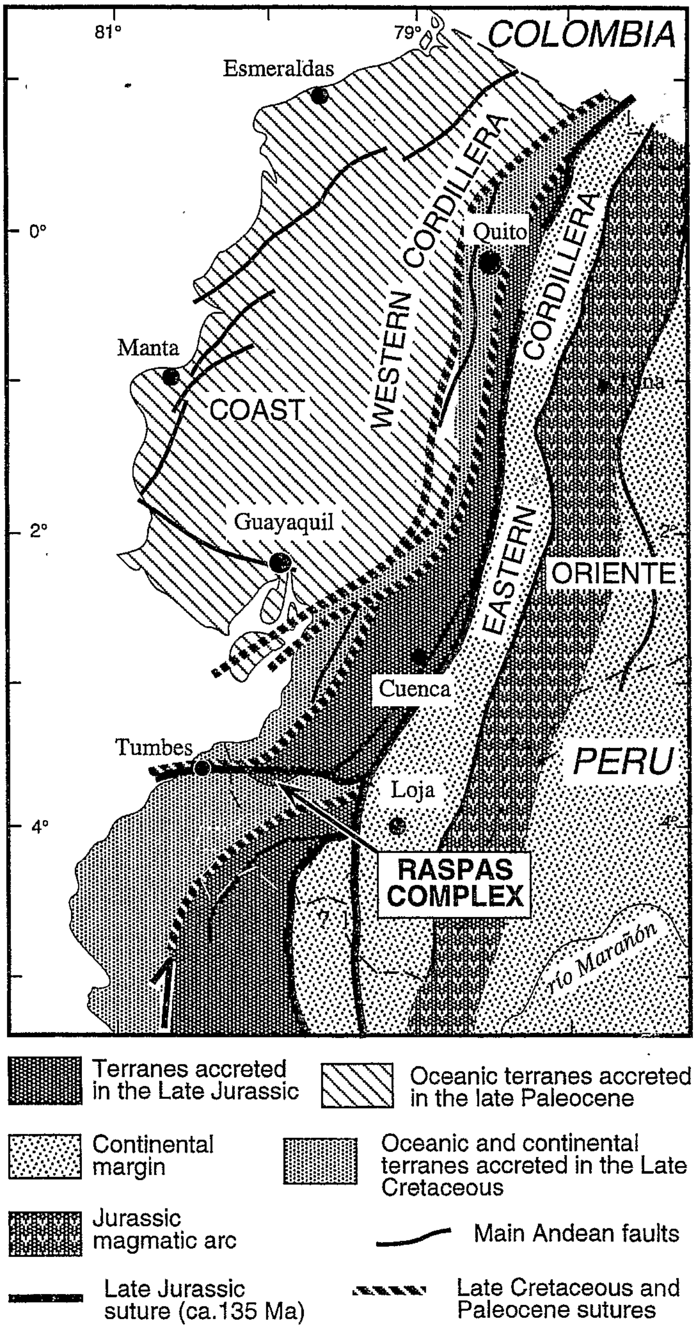

**Figure 1. Outline geologic and terrane map of Ecuador, showing location of Raspas metamorphic complex.**

## INTRODUCTION

During the early Mesozoic, evolution of the margin of northwestern South America was predominantly controlled by suprasubduction-zone tectonomagmatic activity (Aspden et al., 1987; Jaillard et al., 1990). Since the Late Jurassic, however, the evolution has comprised growth through accretion of varied continental and oceanic terranes, modified by dextral, transcurrent slip along north-northeast–striking fault systems (Fig. 1) (McCourt et al., 1984; Litherland et al., 1994). Suturing and subduction of oceanic crust and plateaus (and superposed arcs) occurred during Late Jurassic, Late Cretaceous, and early Tertiary time (Fig. 1) (Litherland et al., 1994; Jaillard et al., 1997). For the past 26 m.y., eastward subduction of the Nazca plate at ~5–8 cm/yr (Pardo-Casas and Molnar, 1987) has been associated with Neogene development of continental-margin-arc-type volcanoes, constructed predominantly on this assembly of accreted terranes (Litherland et al., 1994).

Along the western boundary of the Eastern Cordillera of north-central Ecuador, a major fault system (Peltetec-Portovelo) marks the suture of the Amotape-Chaucha terrane (Litherland et al., 1994) and extends northward into Colombia (McCourt et al., 1984; Kerr et al., 1997). Metamorphic rocks within the extension of this suture in Colombia have ages of 105–160 Ma (Toussaint and Restrepo, 1994). Seismic reflection data indicate that the Amotape-Chaucha terrane has partially subducted peripherally and beneath preexisting Mesozoic continental arc systems (B. Guillier, 1998, personal commun.). Dextral transcurrent motion associated with clockwise rotation (Mourier et al., 1988), concurrent with and subsequent to subduction and accretion of the terrane, has resulted in exhumation of previously subducted parts of this terrane that are known as the El Oro metamorphic complex; part of the El Oro complex comprises an exotic block of eclogite-blueschist-amphibolite known as the Raspas metamorphic complex (Fig. 1). Noble et al. (1997) reported Triassic ages (221 Ma for mafic rocks; 228 Ma for granitoids) in the El Oro complex, correlative with Triassic batholiths of the

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Cordillera Royal. The Raspas metamorphic complex includes a high-pressure ($P$), low-temperature ($T$) suite comprising eclogite, garnet amphibolite, and kyanite-mica-glaucophane schist (Duque and Feininger, 1974; Feininger, 1980; Aspden et al., 1995). Feininger and Silbermann (1982) reported a phengite K-Ar age of 132 ± 5 Ma.

Here we present bulk major and trace element analyses of representative rock types from the Raspas metamorphic complex. We include laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) 50-mm-diameter spot–trace element analyses of eclogitic garnet, together with Sr-Nd (and selected Pb) isotopic analyses of bulk rocks and separated minerals. Through comparison of these data with fresh oceanic (mid-ocean ridge and ocean island) basalts, we suggest the following. (1) The Raspas metamorphic complex includes at least one to three layers of ordinary oceanic crust and underlying mantle lithosphere, together with fragments of oceanic plateaus. Ecuadorian continental growth during the Mesozoic involved incorporation of volumetrically significant oceanic crustal components. (2) Subduction (and exhumation) of oceanic lithosphere has resulted in selective bulk trace element geochemical changes; e.g., Rb, Ba, and Sr have been lost (ranging from ~85% to 50%) from the high-$P$, low-$T$ metamorphosed pelagic sedimentary rocks and basalts, whereas Pb is markedly enriched in mafic rocks. In contrast, U, Pb, and rare earth elements (REEs) were immobile during formation of the eclogite. (3) High-$P$, low-$T$ metamorphosed terranes probably underlie the active continental arc volcanoes of Ecuador. Incorporation by ascending mantle-wedge–derived basalt magmas of partial melts of this basement seems a plausible explanation for the widespread occurrence of adakitic (i.e., high La/Yb and Sr/Y; see Defant and Drummond, 1990) components recognized in the magmas of these volcanoes (Kilian et al., 1995; Monzier et al., 1997).

## RASPAS LITHOLOGIES

About 40 km$^2$ of high-pressure metamorphic rocks (Table 1)[1] enclosed within serpentinized harzburgite, are exposed along the Quebradas Raspas (79°57′W, 3°37′S). Strongly foliated micas interlayered with undulatory-extinguishing quartz laminae surround porphyroblastic garnet in the pelitic schists. Garnet contains inclusions of quartz, rutile, graphite, and kyanite. In eclogites, omphacite and garnet also contain inclusions of other minerals. Rutile and clinozoisite are common in omphacite, whereas rutile, omphacite, and dodecahedrally arranged shells of quartz are present in garnet. Peak metamorphic conditions were in the range $P_{(total)}$ = 1.3–2 GPa (~45–60 km depth) and $T$ of ≤600 °C.

## ANALYTICAL RESULTS

Analytical data (Table 2; see footnote 1) for representative lithologies from the Raspas metamorphic complex are presented for greenschist facies metabasalts, metagabbros, serpentinized harzburgite, mafic garnet amphibolite, eclogite facies metapelites, and basalt. The data comprise (1) trace elements determined by solution and selective LA-ICP-MS for amphibole and omphacite separates and garnet (Table 3; see footnote 1) in thick section from a mafic eclogite; (2) bulk-rock isotopic data ($^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd) for mafic lithologies and mineral separates; and (3) Pb isotopic ratios of the bulk-eclogite and omphacite separates.

The REE$_{CN}$ abundances of the pelitic schists (Fig. 2A) are similar to those characteristic of bulk continental crust (Taylor and McLennan, 1985), a conclusion emphasized by essentially unfractionated (relative concentrations ~1) abundances of the REEs when normalized directly to bulk continental crust in Figure 2D. There is no indication in these high-grade pelitic rocks that bulk or differential selective loss of the REEs has occurred compared with likely protoliths. The absence of selective loss of light compared with medium to heavy REEs is noteworthy. For Sr, however, extensive loss of ~60% is indicated by the negative anomaly in bulk continental crust–normalized abundances. In contrast, bulk continental crust–normalized abundances of other large ion lithophile elements (LILEs) regarded as mobile in fluids in suprasubduction zone environments (e.g., Pearce and Peate, 1995) are undepleted. For example, there is no indication that Rb, Ba, U, and Pb have been lost during metamorphic transformation of the pelitic schists. Rather, it appears that in the case of Pb (and Ba in one sample), the lithologies are relatively enriched.

The range of REE abundances and fractionations (light REE vs. medium REE vs. heavy REE) in the greenschist facies metabasalts and metagabbros are similar to those of N-MORB (normal mid-ocean ridge basalt) associations (Fig. 2B). The gabbros are partly accumulative, with positive Eu anomalies typical of cumulus plagioclase. Given the REE$_{CN}$ pattern (and $\varepsilon_{Nd(T150\,Ma)}$ = +12.2), the protolith of the mafic garnet amphibolite was probably an N-MORB–related cumulate gabbro.

The REE$_{CN}$ abundances of the mafic eclogite are distinct compared with those of other mafic rocks (Fig. 2B). For example, (La/Sm)$_{CN}$ and (La/Yb)$_{CN}$ (1.00 and 1.15, respectively) exceed those of N-MORB (0.61 and 0.59) and approach enriched MORB (E-MORB) ([La/Sm]$_{CN}$ = 1.56; [La/Yb]$_{CN}$ = 1.9) (see Sun and McDonough, 1989) or some large Pacific oceanic plateaus (e.g., Neal et al., 1997). The REE$_{CN}$ abundances of the eclogite are identical to those of oceanic plateau basalts forming the 123 Ma Piñón terrane in northwest Ecuador (Lapierre et al., 1999).

The chondrite-normalized abundances of the medium to heavy REE of the serpentinite are within the general range expected of residual (to basalt extraction) ultramafic lithologies (Fig. 2B). However, two features may reflect original melt veining: (1) enrichments of light REEs relative to medium REEs; and (2) a positive Eu anomaly (Eu/Eu* = 1.76).

The N-MORB–normalized, extended trace element abundances of the varied mafic-ultramafic lithologies are informative (Fig. 2E). For greenschist facies material, excluding Rb and Ba (in one metagabbro) and Pb (in both metabasalts and metagabbros), overall abundances are relatively unfractionated. Although Ba is below the detection limit (<5 ppb) and may have been lost from the serpentinite, there are no apparent losses of Rb, Th, U, and Sr. Likewise, smooth relative enrichments of some LILEs in the eclogite (Th, U, Nb, Ta, and Pb) are consistent with an unfractionated preservation of original E-MORB or oceanic island basalt (OIB) abundances. Conversely, abundances of Rb, Ba, and Sr are significantly depleted compared with fluid-immobile LILEs.

An estimate of depletions of Rb, Ba, and Sr from the eclogite is possible through comparisons of relative abundances reported for Rb, Ba, Th, U, and Nb in E-MORB and OIB by Sun and McDonough (1989). For example, given a normalized abundance of Th in the eclogite of ~4.25 times its abundance in N-MORB, we can predict an abundance of 7–8 times that in N-MORB for Rb and Ba. However, the abundances of Rb (0.55 ppm) and Ba (22 ppm) reflect ~85% and 50% loss, respectively. Compared with elements of similar melt-residue incompatibility (Pr, P, and Nd), there has been ~50% loss of Sr from the eclogite protolith.

A striking feature of Figure 2E, however, is the lack of depletions in the eclogite of Th, U, Pb, and any light REEs to medium REEs relative to elements of similar incompatibilities (e.g., Nb, Ce, and Pr). These data are critical in view of the marked overabundance of Th, U, and Pb, together with Rb, Ba, and Sr in suprasubduction-zone magma types (e.g., Pearce and Peate, 1995). Other measures of consistency of U and Pb in the eclogite compared to Nb and Ce, respectively (elements with identical bulk peridotite-melt distribution coefficients as determined by Hofmann et al. [1986]), are Nb/U = 41 and Ce/Pb = 22.5. In most MORB and OIB samples, Nb/U = 49 and Ce/Pb = 25. Loss of U and Pb in subduction-zone fluids would have increased the ratios.

Furthermore, with respect to potential mobility of Pb, enrichments in serpentinite, metabasalts, and metagabbros (including the garnet amphibo-

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[1] GSA Data Repository item 9946—Table 1, Summary of Raspas metamorphic complex phase assemblages; Table 2, Analytical data for selected Raspas metamorphic complex lithologies; Table 3, Rare earth element abundances of the garnet in eclogite—is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, editing@geosociety.org, or at www.geosociety.org/pubs/drpint.htm.

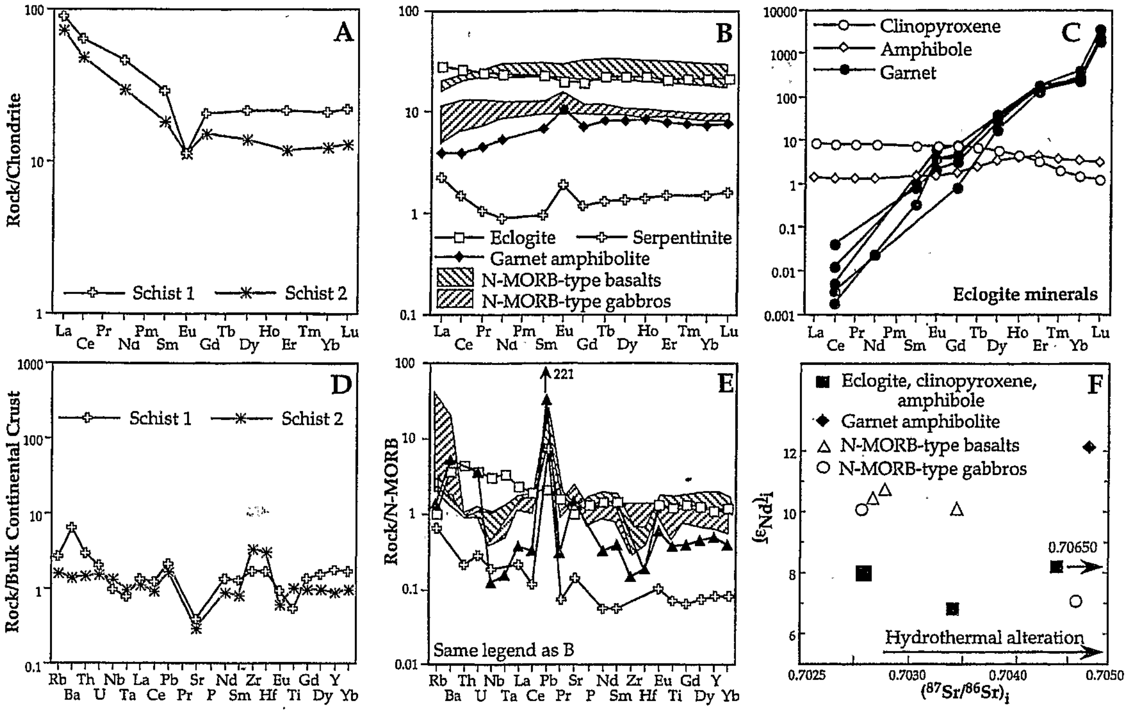

Figure 2. A, B, C: Chondrite-normalized rare earth element abundances in (A) pelitic schists, (B) mafic and ultramafic rocks, and (C) individual minerals of mafic eclogite of Raspas metamorphic complex. D, E: Extended trace element abundances (D) for same pelitic schists as in A normalized to bulk continental crust and (E) same lithologies as in B normalized to N-MORB (same lithologies as B). F: $(^{87}Sr/^{86}Sr)_i$ vs. $(\varepsilon_{Nd})_i$ with initial ratios calculated at 150 Ma, on basis of measured $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ and median age of Amotape-Chaucha terrane. Analytical data reported in Tables 2 and 3 (see text footnote 1).

lite) are dramatic. The mineral host or hosts of Pb in these lithologies are unknown. Although the data may be indicative of Pb mobility during metamorphism, it is also possible that even within the garnet amphibolite and serpentinite, potential mineral sinks exist.

Equilibrium distribution and mass balance of the REEs in high-*P*, low-*T* subduction zone–related rocks is of interest in geochemical modeling of crust-mantle systems. For eclogite facies metagabbros involved in Alpine subduction processes, Tribuzio et al. (1996) showed that major mineral hosts in blueschists are lawsonite (light REEs) and titanite (medium and heavy REEs), compared with allanite (light REEs) and garnet (heavy REEs) in eclogite. During dehydration accompanying prograde metamorphism of sea-floor–altered rocks, development of blueschist and eclogite facies assemblages can be REE conservative in subducted oceanic crust (Tribuzio et al., 1996; Poli and Schmidt, 1995).

For studies of the partial internal distribution of the REEs within the Raspas eclogite (Fig. 2C), clean separates of omphacite and amphibole were obtained by solution ICP-MS, but numerous quartz, clinozoisite, and rutile inclusions in garnet required LA-ICP-MS spot analysis. Overall, distribution of the REEs between garnet, omphacite, and amphibole is controlled by strong enrichments of the heavy REEs in garnet and preferential partitioning of the light REEs in omphacite compared with amphibole. The partitioning preference between omphacite and amphibole is reversed in the case of heavy REEs. It is clear from the whole-rock abundance of light REEs at ~24 times the chondritic abundances (Fig. 2B) that an additional mineral host is required for mass balance, given that chondrite-normalized La in omphacite is ~10. This host is probably clinozoisite (e.g., Poli and Schmidt, 1995). However, despite total internal redistribution of the REEs during prograde metamorphism, the bulk-rock system has remained closed to selective REE losses.

In a plot of $(^{87}Sr/^{86}Sr)_i$ vs. $(\varepsilon_{Nd})_i$ (Fig. 2F) (i = the initial ratio calculated at 150 Ma; $[\varepsilon_{Nd}]_i$ = deviation in $10^4$ from a chondritic uniform reservoir [CHUR] at 150 Ma [= 0.512445]), the majority of mafic Raspas samples project at high $^{87}Sr/^{86}Sr$ ratios compared with the disarray of mantle-derived basaltic magmas (e.g., Hofmann, 1997). Elevated $^{87}Sr/^{86}Sr$ ratios could have resulted from sea-floor hydrothermal metamorphism. More critical are the high $(\varepsilon_{Nd})_i$ values of ~+10 to +11 for the greenschist facies basalts and gabbros, and +12 for the garnet amphibolite facies metagabbro. These values are clearly consistent with a MORB-related genesis. Although whole-rock eclogite has elevated $^{87}Sr/^{86}Sr$ ratios, the high $(\varepsilon_{Nd})_i$ value of +8.3 is also consistent with oceanic crustal genesis. Furthermore, the coupled $(\varepsilon_{Nd})_i$ = +8 and $^{87}Sr/^{86}Sr$ = 0.70307 values for acid-leached omphacite from this eclogite are within the field of OIB. Coupled $(^{87}Sr/^{86}Sr)_i$ and $(\varepsilon_{Nd})_i$ values of the acid-leached amphibole (0.70391 and +6.8, respectively) indicate Nd isotopic equilibrium and Sr isotopic disequilibrium. Partial mineral and bulk eclogite equilibrium may reflect permeation during prograde or retrograde metmorphism by fluids carrying comparatively radiogenic Sr.

Preliminary Pb isotopic data obtained for whole-rock eclogite and acid-leached omphacite are, respectively: $(^{206}Pb/^{204}Pb)_i$ = 18.691 and 18.229 (i calculated at 150 Ma); $(^{207}Pb/^{204}Pb)_i$ = 15.561 and 15.505; and $(^{208}Pb/^{204}Pb)_i$ = 38.249 and 37.934. These data project above the Northern Hemisphere reference line of Hart (1984), an effect commonly attributed to involvement of an enriched mantle component in the genesis of OIB (e.g., mix of EM1 and EM2 [enriched mantle sources] with a MORB-type source). Collectively, systematics of the trace element abundances (e.g., $[La/Yb]_{CN} > 1$) combined with $(\varepsilon_{Nd})_i$ = +8 and relatively radiogenic $^{207}Pb$ and $^{208}Pb$ abundances are consistent with an OIB origin for the eclogite.

## DISCUSSION

The Raspas metamorphic complex constitutes a fortuitously exhumed geochemical window into the partially accreted and partially subducted terranes of western Ecuador and includes components of oceanic crust and underlying lithosphere, together with fragments of oceanic plateaus. Continental growth during the Mesozoic has clearly involved addition of these lithologies.

Subduction (and exhumation) of oceanic lithosphere encapsulated in the complex has resulted in selective bulk trace element changes: e.g., Rb, Ba, and Sr have been lost (ranging from ~85% to 50%) from high-*P*, low-*T* metamorphosed pelagic sedimentary rocks and basalts, whereas Pb (and in some samples, Rb and Ba) is strongly enriched relative to other trace elements of similar melt vs. residue incompatibility in the mafic (greenschist to garnet amphibolite) rocks. In contrast with alkali metals and alkaline earth elements, U, Th, Pb, and the REEs appear to have been immobile in the formation of the eclogite (Bebout, 1996). Because the eclogite still contains hydrous phases (clinozoisite and amphibole), further dehydration at higher pressures than those that affected the complex might release these elements. Amphibole is not a major host for any of these elements (Table 1; see footnote 1), and we have been unable to analyze clinozoisite. Identification of mineral host(s) for U, Th, and Pb in eclogite requires further study. An important conclusion is that mobilization of the trace elements characteristically enriched in arc magmas (alkalies > U, Th, alkaline earth elements, and Pb > light REEs) must be distributed over a pressure range (Poli and Schmidt, 1995), and some (e.g., REEs, U, Th, and Pb) may persist in the solid residue of the subducted slab beyond regions of arc magma genesis.

High-*P*, low-*T* metamorphosed terranes (such as the Piñón and Amotape-Chaucha) probably underlie most active arc volcanoes of Ecuador. Partial melting of basement terranes (of garnet amphibolite and eclogite facies) by ascending mantle-wedge–derived basalt magmas and variable mixing of anatectic adakitic melts (Rapp and Watson, 1995) with basalts are probable. We concur with authors who advocate this type of mechanism, rather than partial melting of subducted Nazca plate, as the most likely explanation for widespread occurrence of adakitic components in active Ecuadorian volcanoes (Kilian et al., 1995; Monzier et al., 1997).

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