

Mantle source of back-arc Ecuador volcanoes: insights from B and radiogenic isotopes

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The Plio-Quaternary Ecuadorian volcanic arc belonging to the Northern Volcanic Zone (NVZ) of the Andes consists of the Western Cordillera (fore-arc), the Cordillera Real (main-arc) and scattered volcanoes in the rear-arc zone. The largest volcanoes of the rear arc zone are the Sumaco and El Reventador. These volcanoes, despite being located at the same distance from the trench, exhibit erupted magmas of different compositions.

The products of El Reventador are mainly represented by porphyritic lavas, ranging from basalt to rhyolite, with basaltic andesite and andesite being the most abundant. They belong to the medium-K to high-K calc-alkaline series. In contrast, the products of Sumaco are markedly SiO₂-undersaturated and vary from basanite to phonolite. Although both volcanoes show Nb-Ta-Ti negative anomalies typical of subduction-related environments, trace element concentrations are markedly different: modest enrichment in incompatible trace elements is typical of El Reventador lavas, whereas the Sumaco products are strongly enriched in all incompatible elements and show quite low LILE/HFSE ratios (i.e. Ba/Nb 35-105). In addition, El Reventador samples exhibit higher ⁸⁷Sr/⁸⁶Sr (0.7044-0.7046) and lower ¹⁴³Nd/¹⁴⁴Nd (0.51272-0.51280) with respect to Sumaco (⁸⁷Sr/⁸⁶Sr ≈ 0.7041-0.7043, ¹⁴³Nd/¹⁴⁴Nd ≈ 0.51284-0.51297). It is worth noting that the Sr-Nd isotopic fields of the two back-arc volcanoes are well within the Ecuadorian NVZ variation range (0.7035 < ⁸⁷Sr/⁸⁶Sr < 0.7047; 0.5126 < ¹⁴³Nd/¹⁴⁴Nd < 0.5130) [1]. Nevertheless, El Reventador Sr isotopic ratios are among the highest values of the Ecuadorian volcanic rocks from literature. The two volcanoes show similar and almost constant ²⁰⁷Pb/²⁰⁴Pb ratios. The other Sumaco Pb isotope ratios (18.738 < ²⁰⁶Pb/²⁰⁴Pb < 18.858; 38.525 < ²⁰⁸Pb/²⁰⁴Pb < 38.594) are comparable with the overall Ecuadorian isotope variations (18.700 < ²⁰⁶Pb/²⁰⁴Pb < 19.150; 38.450 < ²⁰⁸Pb/²⁰⁴Pb < 38.950 [1]), whereas El Reventador lavas have the lowest ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb among all the other Ecuadorian volcanoes (38.408-38.506 and 18.541-18.682, respectively). Even B isotopes are clearly distinct, with δ¹¹B ranging from -1.0 to -2.5 for El Reventador samples and -5.2 to -7.2 for the Sumaco samples.

All of this suggests that the erupted magmas of these rear-arc volcanoes represent two different mantle sources. The Sumaco product's source is consistent with very low degrees of partial melting due to the metasomatization of a supra-slab mantle wedge by small amounts of ¹¹B-depleted fluids released from subducted AOC and sediments. In contrast, under the El Reventador volcano a carbonatic sediment component (with low ²⁰⁶Pb/²⁰⁴Pb and high δ¹¹B) is invoked as significant agent of mantle wedge metasomatization.

[1] Bourdon et al. (2003) *Earth Plan. Sci. Lett.* **205**, 123-138.

Carboxyl group δ¹³C values of naphthenic acids: A novel approach to source discrimination

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Naphthenic acids (NAs) are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids naturally present in bitumen that become concentrated in oil sands process waters (OSPW). Difficult to characterize and quantify, NAs are highly toxic to aquatic organisms and thus pose a significant threat to the environment. Here we report a novel method to isolate and characterize NAs for use in source apportionment studies. NAs were extracted from a range of water samples and isolated into different mass fractions using preparative capillary gas chromatography (PCGC) prior to carboxyl group carbon δ¹³C analysis (δ¹³C_{carboxyl}) by thermal conversion / elemental analysis – isotope ratio mass spectrometry. As the processes involved with bitumen recovery may result in a unique isotopic fingerprint in OSPW, our goal was to understand the variability in δ¹³C_{carboxyl} of NAs in order to determine their potential to discriminate sources.

Results and Conclusion

The δ¹³C_{carboxyl} ratio showed little variation within a given sample, demonstrating no significant isotopic differences between various mass fractions of NAs. The δ¹³C_{carboxyl} value for unprocessed oil sand was -22.6‰ and did not vary considerably from that measured in OSPW (-21.8 ± 0.5‰). These results suggest that δ¹³C_{carboxyl} of NAs cannot be used to distinguish between process-derived and natural background NAs. However, in samples taken along an OSPW-impacted groundwater transect, δ¹³C_{carboxyl} values show a slight yet significant ¹³C-depletion (~3‰) down-gradient away from the source. In conjunction with data from high-resolution Orbitrap mass spectrometry analyses used to identify NAs in these samples, the isotopic results point to a potential contribution from an additional source of “acid extractable” organic matter other than OSPW-derived NAs. This research highlights the need for accurate characterization of naphthenic acids in order to distinguish between anthropogenic and natural organic matter sources.