Understanding the link between tectonic-driven extensional faulting and volcanism is crucial from a hazard perspective in active volcanic environments, while ancient volcanic successions provide records on how volcanic eruption styles, compositions, magnitudes and frequencies can change in response to extension timing, distribution and intensity. This study draws on intimate relationships of volcanism and extension preserved in the Sierra Madre Occidental (SMO) and Gulf of California (GoC) regions of western Mexico. Here, a major Oligocene rhyolitic ignimbrite “flare-up” (>300,000 km$^3$) switched to a dominantly bimodal and mixed effusive-explosive volcanic phase in the Early Miocene (~100,000 km$^3$), associated with distributed extension and opening of numerous grabens. Rhyolitic dome fields were emplaced along graben edges and at intersections of cross-graben and graben-parallel structures during early stages of graben development. Concomitant with this change in rhyolite eruption style was a change in crustal source as revealed by zircon chronochemistry with rapid rates of rhyolite magma generation due to remelting of mid- to upper crustal, highly differentiated igneous rocks emplaced during earlier SMO magmatism. Extension became more focused ~18 Ma resulting in volcanic activity being localised along the site of GoC opening. This localised volcanism (known as the Comondú “arc”) was dominantly effusive and andesite-dacite in composition. This compositional change resulted from increased mixing of basaltic and rhyolitic magmas rather than fluid flux melting of the mantle wedge above the subducting Guadalupe Plate. A poor understanding of space-time relationships of volcanism and extension has thus led to incorrect past tectonic interpretations of Comondú-age volcanism.