The chief concern of this dissertation is to investigate a fundamental, yet unsolved problem within the phonology of Proto-Indo-European (PIE): the process of syllabification. I show that by analyzing the much more easily reconstructable word-edge clusters we may predict which types of consonant clusters can occur word-medially, provided that we assume a special status for certain consonants at word's edge. Having thus analyzed the entire PIE phonological system, I believe I have developed the first working hypothesis of Indo-European syllabification, which we may now use to predict which types of syllable-driven rules of consonant deletion and vowel epenthesis occurred within PIE. My dissertation argues that there existed at least five phonological processes of this type. The second half of the dissertation focuses on the problem of Sievers' Law, through which I argue for the tendency in PIE to keep morphemes syllabically distinct, in accordance with a high-ranking constraint ALIGN. I conclude by proposing that the assumption of morphological relevance in the syllabic derivation provides us with a mechanism to reconcile the well-established principle of ONSET MAXIMIZATION with the reconstructable parsing of VCCV sequences as VC.CV.