Perlites are volcanic glasses of exclusively rhyolitic composition that contain curved fractures around still intact cores of glass. To achieve a more detailed view into the mechanisms controlling formation of fracture networks in volcanic glass and the understanding of microstructures and textures related to perlitic fractures, this study relies on a combination of volcanological and glass technical models supported by stochastic image analysis. The research is based on methodical investigations of 35 rock samples from 24 different locations from five continents (Americas, Eurasia, and Africa) and of different geological ages to cover a broad spectrum of textural variations. The process of perlitization creates a three-dimensional fracture network, which can only be found in rocks comprising elevated H₂O contents. Related studies on rhyolitic textures are sparse and it is widely debated if perlitic fractures form in response to hydration solely or due to thermal stress before hydration. The three-dimensional geometry of the fracture network, which links perlitization to a three-dimensional (paleo)strain field, was proven by computer-tomography measurements. Further investigations on the fracture network show that perlitic cracks form secondary and are always accompanied by primary sublinear quench fractures. The prevalent relation between the two discrete fracture sets is also determined by stochastic image analysis. It was additionally found that crack propagation is further advanced in old samples and ignimbrites because of longer elapsed time spans for crack propagation and the compaction of the glass itself. Crack propagation is supported by the presence of H₂O and increases with time whereby certain samples show several generations of perlitic fractures. Besides transmitted-light microscopy, the study includes electron microprobe- and thermal analysis techniques (DSC/TG analysis) to gain insights into fluid- and elemental compositions and mobilities. Pre-Cenozoic fully hydrated samples show no variations in fluid content between rim and core but an effect of differential depletion or enrichment can be observed, whereas younger samples with unbalanced water contents indicate incomplete hydration, which reveals a direct connection between alkali mobility and hydration of a rock. Perlitization is widespread in rhyolitic reservoirs and the fractures frequently amount to an important fraction of the total porosity. Porosity and permeability measurements were conducted to provide an insight into pore space characteristics. It is shown that they can be either improved or deteriorated through post-volcanic, low-temperature alteration processes, especially abundant in pre-Cenozoic samples. Volcanic glasses are not only important as prolific reservoirs in the oil and gas industry, as they often provide storage capacity in geothermal reservoirs and boast various other applications. It is found that perlitic fractures can form by thermal shock at temperatures just below glass transition temperature, but crack propagation and initiation of subsequent generations of rounded cracks is most likely linked to strain which is induced by continued hydration of a volcanic glass.