Geophysical Research Abstracts
Vol. 16, EGU2014-15131, 2014
EGU General Assembly 2014

Phonolite-hosted zeolite deposits in the Kaiserstuhl Volcanic Complex, Germany

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Several subvolcanic phonolitic intrusions occur within the Miocene Kaiserstuhl Volcanic Complex (KVC) located in the central-southern segment of the Upper Rhine Graben, which is part of the European Cenozoic Rift System. Hydrothermally altered phonolitic rocks are of economic interest, due to the high (>40 wt%) zeolite content, which accounts for the remarkable zeolitic physicochemical properties of the ground rock. These properties have widespread industrial application in water softening, catalysis, remediation of soils and soil quality, wastewater treatment, and as additive in the cement industry. Currently the largest phonolite intrusion Fohberg is active in mining, located in the eastern part of the KVC. The Endhale phonolite, approximately 1.5 km to the north marks a further deposit currently under exploration. Both phonolites are hosted in Tertiary sedimentary units.

The aim of this study is to carry out a new mineralogical and geochemical data a) to evaluate the manifestation of hydrothermal alteration of the Fohberg and Endhale phonolitic intrusions, and b) to constrain the physical and chemical properties of the fluids, which promoted hydrothermal replacement of primary igneous minerals. The high degree of alteration is in contrast to the only slightly altered Kirchberg phonolite in the western KVC. The alkaline intrusive bodies are characterized by the primary mineralogy: feldspathoid mineral, K-feldspar, aegirine-augite, wollastonite, and andradite, with additional REE-minerals (e.g. götzenite). Fluid-induced re-equilibration of feldspathoid minerals and wollastonite caused breakdown to a set of secondary phases. Feldspathoid minerals are totally replaced by secondary phases including various zeolite species, calcite, and barite. Wollastonite breakdown results in the formation of various zeolites, calcite, pectolite, sepiolite, and quartz. The large variability of secondary minerals indicates a heterogenic fluid composition throughout the phonolitic intrusions and through time. Zeolites formed during sub-solidus hydrothermal alteration under alkaline conditions and completely replace feldspathoid minerals in the matrix of the rock. A sequence of Ca-Na dominated zeolite species (gonnardite, thomsonite, mesolite) is followed by pure sodium endmember species (analcime, natrolite). These sequence reflects an increase in $\log[aNa^{+})/(aH^{+})]$ of the precipitating fluid. In contrast to the Fohberg phonolitc the Endhale phonolite contains analcime in addition to natrolite as pure Na zeolite species. The appearance of analcime is caused by higher silica activity during fluid rock interaction, which favors the formation of analcime over natrolite. The Fohberg phonolite is cut by fractures, which are totally or partially sealed with secondary minerals. Secondary minerals contain zeolites, followed by calcite and a variety of other silicates, carbonates, and sulphates as younger generations. Stable isotope analyses of late fracture calcite indicate the late circulation of meteoric fluids and mobilization of organic matter from surrounding sedimentary units.