Zeolite-group minerals in phonolite-hosted deposits of the Kaiserstuhl Volcanic Complex, Germany

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ABSTRACT

Subvolcanic phonolite intrusions of the Kaiserstuhl Volcanic Complex (Germany) show variable degrees of alteration. Their secondary mineralogy has been characterized by petrographic textural observations, bulk-rock powder X-ray diffraction, thermogravimetry, differential thermal analysis, and electron probe microanalysis. The alteration assemblage is dominated by various zeolites that occur in fissures, vugs, and as replacement products of primary phases within the phonolite matrix. Phonolites in the eastern Kaiserstuhl were emplaced into a sedimentary sequence and are characterized by high zeolite contents (Endhalden: 48 wt%, Fohberg: 45 wt%) with the temporal sequence: ± thomsonite–Ca ± mesolite – gonnardite – natrolite – analcime. In the western Kaiserstuhl zeolite contents are lower (Kirchberg: 26 wt% or less) and the crystallization sequence is: ± thomsonite–Ca – gonnardite – natrolite – chabazite-Ca. Pseudomorphic replacement textures and barite inclusions in secondary aggregates suggest that zeolites grew at the expense of a sulfate-bearing sodalite-group mineral, i.e., haüyne. Fresh grains of sodalite-haüyne are only found at Kirchberg, whereas the pervasive alteration at Fohberg and Endhalden transformed feldspathoid minerals completely to zeolites.

Zeolites formed in a continuously cooling hydrothermal regime after emplacement and solidification of phonolitic magmas. The common paragenetic sequence corresponds to a decrease in the Ca/Na ratio, as well as an increase in the Si/Al ratio with time. The shift from Ca-Na to pure Na-zeolites is an expression of closed-system behavior in a water-rich environment at Fohberg and Endhalden, which both intruded an Oligocene pre-volcanic sedimentary unit. The late crystallization of K-bearing chabazite-Ca points to a progressively more open hydrothermal system in the Kirchberg phonolite, which was emplaced in a subaerial volcanic succession and was influenced by K-enriched fluid from leucite-bearing country rock. Therefore, the geological setting and nature of emplacement are important factors that control the degree of zeolitization of intrusive feldspathoid minerals-bearing rocks and whether a zeolite occurrence can be used as mineral deposit.

Keywords: Natrolite, gonnardite, analcime, zeolite, alkaline rocks, phonolite, Kaiserstuhl; Microporous materials: Crystal-chemistry, properties, and utilizations

INTRODUCTION

Rock alteration and the formation of secondary mineral assemblages are important processes in the genesis of many types of mineral and ore deposits. In fact, most natural zeolite deposits are the result of decomposition of various primary phases in the presence of aqueous fluids. Differences between zeolite deposits exist regarding modal abundances and the mineralogical complexity of the alteration assemblage, from near-monomineralic to highly diverse, which reflects inherent differences in the reacting source rocks, in fluid accessibility and composition, in thermal regime, and in geologic setting (e.g., de’Gennaro and Langella 1996; Ibrahim and Hall 1996; Langella et al. 2013; Weisenberger et al. 2014; Cappelletti et al. 2015; Atanasova et al. 2017).

Natural zeolites form a large group of tectosilicate minerals characterized by the common feature of an open framework structure enclosing interconnected pores and channels. The three-dimensional framework is built of SiO₄ and AlO₄ tetrahedrons in varying proportions but maximum AlO₄ is limited to unity with SiO₄ according to Loewenstein’s rule (Loewenstein 1954). As a consequence, the aluminosilicate framework contains excess electrons and the walls of zeolitic pores and channels are negatively charged, which allows positively charged ions or bipolar molecules to be fixed in this pore space. Due to the weak bonding strength, these ions and molecules are easily exchanged and replaced by others. The most common extra-framework species in natural zeolites are Na⁺, K⁺, Ca²⁺, and H₂O, but several other species, mainly alkali and alkali earth metals and NH₄⁺, are also known to be incorporated. Over 80 naturally occurring zeolite species are defined by Coombs et al. (1997), and over 170 known framework types of natural and synthetic zeolites are illustrated by Baerlocher et al. (2007).

Due to their structure-related physicochemical properties, natural zeolites are an important group of industrial minerals. Technical applications are generally related to their ion-exchange capacity, their reversible dehydration, their regular pore spacing, and their pozzolanic activity, which leads to various applications,