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Mineralogical and paragenetic investigations of cavity filling minerals
and sedimentary xenoliths in basalts from Bakony – Balaton Highland
Volcanic Field

Theses of doctoral (PhD) dissertation
by
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Introduction, aims

The history of studying the appearance and the formation of cavity filling minerals of basaltic rocks constituting the majority of the Earth's crust dates back for over a century. Former researches revealed that the primary minerals (olivine, pyroxenes, plagioclases and oxides) and the rock glass transform into phases metastable under low temperature in the course of hydrothermal processes. Due to the hydrolysis of primary minerals significant amount of chemical elements is released into water solutions from which secondary minerals like clay minerals, zeolites, carbonates \pm silica minerals are precipitated. Smaller-or-greater differences between the appearance of cavity filling minerals of different regions are the results of local processes (e.g. water/rock interrelationship, pH, rock composition, solution composition, etc.).

In the Bakony – Balaton Highland Volcanic Field (later BBHVF), the largest basalt volcanic area of the country rock mining enabled the study of cavity filling minerals and rock inclusions of basalts. Initial works produced scattered data on the minerals of the area. Detailed researches were carried out by Béla Mauritz and János Erdélyi between the 1920s and 1950s. As a result numerous new mineral species were reported in the mineral association of the Balaton Uplands and clearing of the processes discussed above were also advanced. Following this period cavity filling mineral and xenolith research declined significantly due to mine closures and decreasing support.

More than half a century after the research of Béla Mauritz, detailed study of the cavity filling minerals and rock xenoliths of sedimentary origin in the BBHVF was carried out in relation to the intensifying topographic mineral researches covering a certain region or major mine.

The fundamental and primary aim of this work was the detailed mineralogical-genetic examination of the cavity filling mineral association and rock xenoliths of sedimentary origin of the individual sites.

In the first part of the work the mineral composition of the given types of sedimentary rock inclusions, the element composition of the minerals and the formation processes of the mineral associations of the xenoliths are presented. In the second part the cavity filling (miarolitic and hydrothermal) minerals are discussed (appearance, element composition, grade of ion substitutions). Considering the latter, I have regarded the study of zeolites the most important as chemical composition and zonality of which very little information is available. One chapter at the end of the work discusses the relationship between the appearance of zeolites and the alteration types of basalts (sunburn and coccolithic) and their importance in practice regarding mining and the building industry.

Actuality of the problem is given also – apart from the above – by the establishment of the Bakony–Balaton Geopark. Because of this research in the area was extended significantly in the last two decades. By 1999 the geological map and explanation of the Balaton Uplands was constructed and by 2004 the volcanism of the area was reviewed in the light of the new international models. Detailed mineralogical investigations, however, have not yet been performed. Complementing this – associated to the geology – further contributed to the detailed knowledge of the Balaton Uplands.

Applied methods

Analyses were performed on samples collected in the last 4 years and provided by mineral collectors and museums (Mineral Museum, Eötvös Loránd University – ELTE; Mineral Museum, Herman Ottó Museum – HOM; Geological Institute of Hungary – MÁFI; Department of Mineralogy and Petrology, Hungarian Natural History Museum – MTM).

First stereomicroscope examination was performed on the samples in the X-ray Laboratory of the MÁFI and in the Mineral Museums of the HOM, MTM and ELTE in order to determine the paragenetic series. In order to determine uncertain or doubtful mineral phases X-ray diffraction analyses were performed and in the case of smectites these were supplemented by orientated preparation investigations and thermal analyses (Thermal Laboratory, MÁFI). In order to determine the valence state of the iron in the smectites Möessbauer-spectroscopic analyses were performed in the Department of Nuclear Chemistry, ELTE.

Chemical analyses without standards were performed on the mineral phases of the carbonaceous and serpentinitic inclusions by the JEOL 8600 SX Superprobe instrument of the Department of Mineralogy and Petrology, University of Miskolc and on quartz inclusions by the AMRAY-1830 I/T6 instrument equipped by an EDAX PV 9800 energy dispersion X-ray spectrometer of the Department of Petrology-Geochemistry, ELTE. Analysis of the fluid inclusions observed in quartz crystals of the sandstone inclusions was performed by a Nikon Eclipse E600 microscope equipped by a THMSG 600 heatable-coolable stage.

Wave-length dispersive (WDS) analyses of the zeolites were performed by the ARL-SEMQ instrument equipped by four WDS detector in the Department of Earth Sciences, University of Modena with the following standards: Sr-anortite for Sr, AN80 for Ca, Albite Amelia for Na and Al, Microcline AB for K and Si, Olivine P140 for Fe and Mg, Paracelsiane for Ba. For zeolite species I calculated formula equilibrium error according to the following relationship: $E = [(Al + Fe - Al_{theor.}) / Al_{theor.}] \cdot 100$, where $Al_{theor.} = (Na + K) + 2(Ca + Mg + Ba + Sr)$. Chemical composition of the given zeolite species can be applied if $E < 10\%$. Positive error indicates the excess of trivalent while negative error signs the excess of substitutable cations. Apart from these thermal analyses and infra red investigations were performed on the minerals of the natrolite group in order to determine structural differences. I carried out the latter examination by the Perkin-Elmer–1600 Fourier transformation Spectrophotometer of the Infra Red Spectroscopy Laboratory of the MÁFI in KBr pastilles in the range of $400\text{--}4000\text{ cm}^{-1}$.

Complete chemical analyses (major element, trace element, rare earth element) on the samples from the transition zone were performed in the Chemical Laboratory of the MÁFI. Major element determination was carried out by inductive coupled plasma atomemission spectrometry (ICP-AES, JY 70 simultan sequential ICP emission spectrometer) solution, multi element spectrometry method. One part of the trace elements (As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn) was also determined by ICP-AES while the rest of them were determined by ICP-MS (VG Elemental PlasmaQuad II STE ICP mass spectrometer).

On twelve calcite samples $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ stable isotope analyses were performed in the Laboratory of Environmental Studies, Institute of Nuclear Research, Hungarian Academy of Sciences. Measurements were carried out using a Delta plus XP Thermo Finnigan stable isotope ratio measuring mass spectrometer. Coal values and oxygen values are presented in ‰ as compared to the VPDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water) standards respectively. Chemical analyses of the calcites were performed by a HORIBA Jobin Yvone XGT-5000 microfluorescent spectrophotometer at the Department of Mineralogy, Geochemistry and Petrology, University of Szeged.

New scientific results

1. Based on the occurrence of Mg–Ca silicate rock xenoliths I stated that the inclusions are associated with the phreatomagmatic volcanism having a thick Main Dolomite basement. Rock pieces were altered following contact metamorphism (800-1000 °C) then they were clay mineralized and serpentinized by hydrothermal (230-140 °C) processes.
2. Studying carbonate-silicate xenoliths revealed that alteration of xenoliths started above the temperature of ~900 °C and it was closed with the formation of zeolites at the temperature of 50-100 °C. CaO content of calcium containing mineral phases decreased from 40-50%. To ~10%. Mineral formation could have happened at pressures of 0.5-2 kbar. Inclusions may have originated from the Triassic limestone of the basement.
3. Examinations on quartz xenoliths revealed that the xenoliths may have been formed at temperatures above 870°C. Large size of the xenoliths and potassium feldspar containing melt zone suggest slow cooling. xenoliths were affected by later hydrothermal processes. Xenoliths are probable originated from the sandstone formations composing the basement (e.g. Balatonfelvidék Sandstone Formation).
4. Clayed xenoliths are mainly associated with the phreatomagmatic volcanism. Their mineral phases were formed in two temperature ranges. High temperature minerals occurring in small quantity were formed at temperatures between 500°C and 800°C while those phases formed in the course of hydrothermal alteration were formed at temperatures between 50°C and 230°C. Xenoliths may have originated from the formations of high clay content composing the basement of the volcanoes.
5. In the majority of the basalt-cavity alteration zone, known less even in international terms, pseudo-pegmatitoid texture was observed suggesting a stagnating almost constant melt composition. Nephelin→zeolite and pyroxene, biotite, volcanic glass→smectite alterations occurring in the zone are caused by low intensity hydrothermal melts based on the major and trace element content.
6. Based on the thermal analysis of smectites associated with the cavity filling and Mg–Ca-silicate inclusions in Uzsa it can be stated that Mg ion dominates in the interlayer space of the minerals and Ca ion is subordinate. Such smectites are associated with the basalt volcanoes having thick Main Dolomite basement.
7. In zeolite mineral series using wave length dispersive electronmicroscope analyses I was the first to detect the mineral species of phillipsite-Na, chabazite-K, chabazite-Na, gmelinite-Ca and gonnardite-Na in Hungary and phillipsite-K in the Balaton Uplands.
8. Chabazite-Mg was identified as a new zeolite species that was formed from Mg containing melts in the presence of aragonite and smectite (saponite). Symmetry of chabazite-Mg is trigonal rhombohedral (R-3m). Its formula based on 17 WDS analyses is the following: $(\text{Mg}_{0.67}\text{K}_{0.52}\text{Ca}_{0.48}\text{Na}_{0.08}\text{Sr}_{0.03})[\text{Al}_{3.16}\text{Si}_{8.89}\text{O}_{24}] \cdot 9.51\text{H}_2\text{O}$, its simplified formula is: $\text{Mg}_{0.75}\text{K}_{0.50}\text{Ca}_{0.50}(\text{Al}_3\text{Si}_9\text{O}_{24}) \cdot 10\text{H}_2\text{O}$. Data of the mineral are currently submitted to the International Mineralogical Association, Commission on New Minerals and Mineral Names.

9. Zeolites with chemically homogeneous chain structure are less frequent in vesicles. Within a pin Ca and water content decreases generally towards the top of the pin. Zonality can be observed both perpendicular and parallel to the 'c' axis.
10. Within the natrolite group more mineral species and more pins of homogeneous composition were detected in the radial – sheaf like heaps. Gonnardite dominates in spherical aggregates. Based on zeolite associations the composition of the spherical type is more homogeneous.
11. I was the first to apply thermal analytic corrected decomposition temperature and activating energy on the minerals of the natrolite group in Hungary. According to my investigations these correlate with the grade of Ca substitution in the lattice.
12. On the basis of the distribution of minerals the following correlations were observed:
 - 12.1. At the given sites based on the calcite/phillipsite ratio I observed that few/less phillipsite were formed from Ca^{2+} containing melts in the case of calcite formation while few/less calcite were formed from these melts in the case of phillipsite formation.
 - 12.2. Ca^{2+} ions incorporated into the lattice of gonnardite and calcite reduce the possibility of scolecite formation.
 - 12.3. Formation of offretite does not help the occurrence of phillipsite and natrolite. Its most frequent accompanying minerals are smectite and aragonite.
 - 12.4. In the case of nepheline and/or sodalite crystallization in miarolitic mineral association as Na^+ ions are later hydrothermal effects will not produce natrolite or only in very few cavities.
13. I separated two sections of zeolite formation. Analcime and leucite occurring together with the miarolitic minerals were formed at a temperature of 250°C. The rest of the zeolites were formed at temperatures between 50°C and 100°C.
14. Formation of cavity filling calcites can be separated into two sections (I. cooling → slight degassing; II. cooling→significant degassing) they are the products of hydrothermal fluids.
15. Formation of cavity filling minerals is dissected into four sections with the decrease of temperature: I. miarolitic minerals, II. Minerals of alteration zones, III. Hydrothermal minerals: III/a. clay minerals, III/b. carbonates, III/c. zeolites, III/d other late forming minerals, IV. epigene minerals. Formation of minerals in section III cannot be separated sharply, overlaps are frequent.
16. Based on the investigation of three basalt types (fresh, sunburn and coccolitic) in the basalt mine at Uzsa I stated that the alteration of the rock depended on the appearance specifics of the zeolites. In the mine the most altered basalt type occurs next to the former tuff ring (wet environment) while the least altered one occurs near the vent. The rock type is in close correlation to the water content of the erupted lava, the quantity of zeolites and the petrophysical parameters.