

AMYGDALOIDAL BASALTS TO ZEOLITES OF THE “SERRA GERAL” FORMATION OF PARANÁ BASIN: POTENTIAL AGRONOMIC USE

Magda Bergmann¹

Carlos Augusto Posser Silveira²

Rodrigo Bandeira³

Adilson Bamberg²

Rosane Martinazzo²

Matheus Grecco⁴

Omid Afzalalghom and Michelle Ottmann (Translators)⁵

Abstract

The amygdaloidal basalts of the “Serra Geral” formation in Rio Grande do Sul, Brazil, were studied in several blocks, which were defined throughout the state, with the aim of determining the different types of zeolites, the varieties present and the lateral persistence of the mineralizations, as well as its approximated quantification. Samples were sent for agronomic tests.

Key Words: Zeolites, basalts, “Serra Geral” formation, agronomic use of zeolites.

Introduction

The zeolites are aluminum, calcium and sodium tectosilicate minerals, with a structure characterized by one or more pore systems, which can constitute interconnected canaliculi. The high capacity of cation exchange, the potential for gas and vapor absorption in their crystalline structure and the ability to act as “molecular sieves” give to this family of minerals a wide variety of uses. The zeolites are used in industrial production systems, livestock, agriculture, and as a way to control and minimize the emission of pollutants. They are also used for producing similar high-cost synthetic materials that are designed for specific uses.

¹ Companhia de Pesquisa de Recursos Minerais/CPRM – Serviço Geológico do Brasil, Rua Banco da Província 105, 90840-030, Porto Alegre RS. magda.bergmann@cprm.gov.br; ² Embrapa Clima Temperado, BR 392 Km 78, CP 403, 96010-971, Pelotas, RS. augusto.posser@embrapa.br; adilson. bamberg@embrapa.br; rosane.martinazzo@embrapa.br; ³ Acadêmico do curso de Geologia IG UFRGS. rodrigo.bandeira@ufrgs.br.; ⁴ Acadêmico do Curso Engenharia Geológica – UFPEL. grecco. eg@hotmail.com.; ⁵ Remineralize the Earth (<http://remineralize.org/>)



The economic exploitation of zeolitic minerals is currently focused on diagenetic deposits, in coastal and marine lagoon sediments, and in volcanic glass alterations. The concentration and utilization technologies are defined for the most common varieties in these environments such as clinoptilolite, mordenite, heulandite and analcime. The zeolites' occurrence in the volcanic rock cavities of the “Serra Geral” formation is cited since the 50’s. However, its exploitation on a commercial scale has never been considered, because of the difficulty in separating the rock matrix, as well as the several different species of zeolites found in the paragenesis of amygdaloidal zones in the volcanic rocks that are distributed over the entire length of the “Serra Geral” formation, in S, SE and Center-W of Brazil. The fieldwork of Project “Agrominerais Bacia do Paraná no Rio Grande do Sul” (Brazilian Geological Survey - CPRM) are identifying a large amount of zeolites in different environments of the “Serra Geral” formation in RS state, with levels that may occasionally characterize entire deposits.

This article shows a brief characterization of occurrences already raised on several blocks of Rio Grande do Sul (RS) state, and debates the potential and agronomic use of zeolite-bearing amygdaloidal basalts of the “Serra Geral” formation in the state that may occasionally also contain calcite.

Materials and Methods

The survey of zeolite occurrences was made using lithostratigraphic profiles, focusing so far on the main prospects, which are clusters of lobes from the Fácies Gramado of the “Serra Geral” formation. These clusters are overlaid on the Botucatu sandstone and the flow-top breccia in the western region of Rio Grande do Sul. The fieldwork was carried out using kappameter and gamma-ray spectroradiometry for lava flow correlation, and comprises extensive sampling intended for laboratory procedures and agronomic tests.

The recognition of zeolite minerals takes several steps, and it has as the main element the macroscopic identification in the field and the order of deposition of different mineral phases in the cavities. This procedure is followed by sample preparation (grinding) in order to be read in the spectroradiometer (*Field Spec*), as well as, in the diffractometry and EDS. The last two methods are used only with selected samples. On the other hand, the zeolites quantification in amygdaloidal basalts is attempted in the field with a detailed description of mineral shapes, frequency range of dimensions and the cavity proportions in the basaltic matrix, in contrast with comparative percentage charts.



The thickness of carrier levels was also investigated, as well as their lateral continuity. Other methods that will be tested are quantification of areas in image processing with ENVI software, regarding pictures of outcrops and blocks cut in three dimensions. The maps of distribution of mineralized horizons and other final cartographic products of the ongoing project will be prepared in the GIS environment.

Zeolites occurrences in the basalts of Rio Grande do Sul

Besides quartz, chalcedony, carbonates and clay minerals of the smectite and zeolite family, zeolites are very common minerals in the parageneses of cavity filling in lava flow tops of “Serra Geral”, with greater variety of species recognized in the basic flows (Simas et al. 1999, Frank et al. 2006, Frank 2008, among others). The cavities' mineralization is a result of fluid percolation through the basalts after their crystallization, commonly associated in the geological literature with tardimagmatic fluids and other solutions generated during the emplacement of the flows overlaid on the volcanic pile (Farjallat e Suguio 1966, In: Frank 2008), as well as to the meteoric waters.

The identification of ridges and remnants of zeolitized sandstone between basaltic lobes, cavities on flowtops filled by sand, as well as partly zeolitized sandstone intrusions, which are common in the basalts of “Serra Geral”, lead us to assume that part of the silicate necessary for crystallization of zeolites may be obtained from the sandstone. Therefore, the recognition of zeolitization in intertraps of Botucatu sandstones lead to the genesis models of sedimentary zeolites, more specifically those from lakes of desert regions, where water has an alkaline nature, high salinity and it is trapped in sediments with volcanic contribution allowing the diagenetic crystallization of zeolites (Surdan 1981). It is most likely that the contribution of the Guarani aquatic system with its calcium-alkaline water is one of the factors to be considered in the genesis of zeolites basalts, since the charge introduced by the flows in unconsolidated sand dunes surely promoted significant settlements in the phreatic aquifer at the time of the first flows. This and other hypotheses have been considered in more recent studies, because they add new visions regarding the process of formation and filling of mineral cavities by silicate and zeolites in the volcanic mines of “Serra Geral”, according to Hartmann et al. 2011.

Thus, among the large number of occurrences of zeolites in amygdaloidal basalts, identified in several environments of the “Serra Geral” formation in RS, it stands out for its abundance and variety of species in the large zone of contact between Botucatu sandstone and the first basaltic flows. This area is continuous along the whole *cuesta* that is designed by them. The partitioning of this larger domain considered the typology and the parageneses of those agrominerals, which defines the blocks of Northern Coastal Area (N), Metropolitan Area of Porto Alegre, Central and Western Border (W), Figure 1.

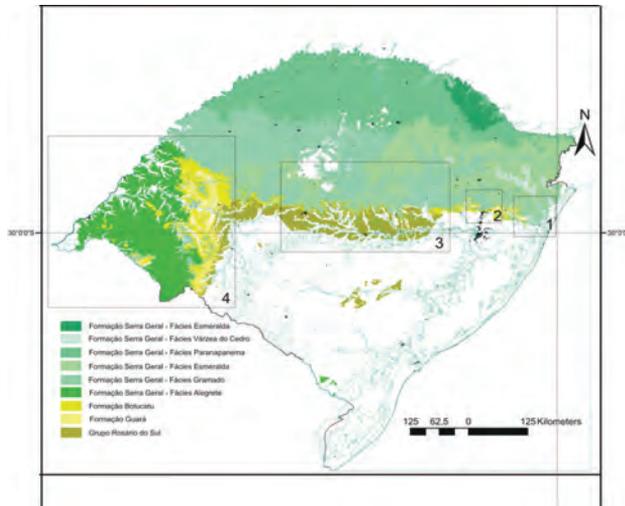


Figure 1. Position of blocks determined by the research along the Botucatu and Serra Geral formation: Northern Coastal block (1) Metropolitan Area of Porto Alegre block (2), Central block (3) and Western Border block (4). Adapted from geological map of Rio Grande do Sul, scale 1:750.000. CPRM/MME.



Results and Discussion

The results obtained by the project “Agrominerais Bacia do Paraná no Rio Grande do Sul” are partial, and at first the parageneses mentioned for the agrominerals of the various blocks are based on bibliographical references and on macroscopic identification of mineral species. These are predominant phases in the outcrops and they will probably be the minerals to be characterized. Due to the large number of samples we have chosen the spectroradiometry method to make the preliminary mineral analyzes, which will need further validation of results.

Bearing these restrictions in mind, the characterization of the various blocks is as follows:

Northern coastal Area of Rio Grande do Sul block

This block has extensive cuts exposed in mines for clay and gravel between “Santo Antônio da Patrulha” and “Maquiné”, plus the cuts in the highway BR 290 (Free Way), BR 101, RS 30 and “Rodovia do Sol”. The prevailing ambience along the block is of the edges of the pahoehoe lava flows from “Fácies Gramado”, creating stacks of P-type and S-type lobes, metric to submetric, with large amounts (up to 30%) of cavities of 1-2 cm and subcentimetric, filled with zeolite. Lobes were alternated with rocks of hypocrySTALLINE tendency. Discontinuous and thin levels of sandstone, often zeolitized, are common among the lobes. The group reaches a thickness of up to 100 m, between “Maquiné” and “Rolante”, and it is overlaid by the first acidic flow, outcropping at varying points along the block. Domical features are associated with acidic rocks in some locations, Figure 2.

The most common paragenesis observed in the block is **laumontite, scolecite and heulandite**, with minerals from the silica and calcite family very subordinate. The laumontite associations, stilbite-stellerite, heulandite and scolecite-mesolite in the basaltic lobes of “Pedreira Britel”, located at “Morro Alto”, are described as secondary minerals by Frank et al. (2008), as well as chabazite, calcite, dolomite, clay minerals, carbonates of Mg, Fe and Mn, goethite and Mn oxides.

Metropolitan Area of Porto Alegre block

The block is defined by the contact of lobes from “Fácies Gramado” with Botucatu sandstones in the region of Novo Hamburgo, Morro Reuter, Picada Café, and in the north part of Taquara, among other places. The lobe stacks have a configuration similar to those of the “Litoral Norte” block, with intertrappean sandstones, and high incidence of sand intrusions that reach tens of meters in the group. The lobes are well exposed in mines for basaltic clay, where they consist of the very material being mined, since their state of decay due to weathering facilitates the extraction. The parageneses observed in the region include **scolecite, laumontite and heulandite**, as well as minerals from the silica and clay mineral family. The centimetric crusts of scolecite and laumontite observed between the lobes stand out, resulting in part from sandstone zeolitization. Dresch (2010) mentions scolecite, heulandite, stilbite, and chabazite, plus chalcedony and celadonite in two gravel pits in “Picada Café” and “Morro Reuter”, Figure 3.



Figure 2. Amygdaloidal basalt containing scolecite and heulandite in lobe of gravel pit in “Picada Café”. Note the residues of partially zeolitized pink sandstone.

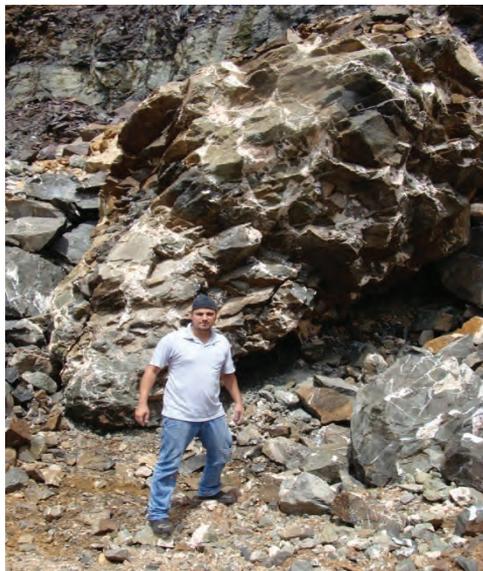


Figure 3. Breccias cemented by laumontite in contact with basaltic lobes and acidic flow. José Inácio quarry, Morro Redondo.

Central block of Rio Grande do Sul

This block is defined in the central portion of the state of RS, with profiles carried out between the rocks of “Grupo Rosário do Sul” and the acidic flows from “Fácies Caxias”, that directly overlap a group of vesiculated lobes of “Fácies Gramado”. In the central portion of this area (Santa Cruz do Sul, Candelária, Vale do Sol), the “Botucatu” sandstones are restricted to a few forms of layers of Aeolian dunes, overlapping the Triassic sediments and forming yet more expressive stacks in the region of “Santa Maria”.

On the other hand, the observations made in gravel mines on the northern and southern outskirts of Santa Cruz do Sul reveal another context of zeolite occurrences associated with an a'a flow top, the first of the local sequence of “Fácies Gramado”.



The sequence of lobes with individual metric to submetric thickness with deepness to N, is position and above a thin interval (a few meters) of the “Botucatu” sandstones, that have features of columnar disjunction due to the thermal effect of the lavas, as well as being strongly disturbed and disrupted by gravitational failures. The thickness of the stack reaches up to 200 m in the sections of BR 153 highway, between Vale do Sol and Herveiras, comprising dominant paragenesis of heulandite, scolecite, clay minerals and calcite, with subordinated silica and mordenite (Figures 4 and 5).

An intertrappean interval occurs above the first lobe, with a small preserved dune, exposing sandstones similar to the “Botucatu” formation, partly zeolitized. This lobe is intensively injected by sandstone dikes, which also percolate the fractures oriented in various systems.



Figure 4. Detail of heulandite-bearing amygdaloidal basalt in exposed lobe in the BR 153 highway.



Figure 5. Aspect of alternating metric and submetric lobes in a section of the BR 153 highway. Note the more oxidized lobes and light zones (zeolite-bearing crusts and venules).

The occurrences of zeolites in the environment of a'a flows are exposed in mines of "Ouro Preto", north of the urban area of Santa Cruz do Sul, and in the southern outskirts (mines of "Fátima" and "Linha Frai" neighborhood), where there is correlation throughout at least 3 Km².

The paragenesis preliminarily recognized includes **stilbite, heulandite, scolecite, calcite and mordenite, plus clay minerals and chalcedony** in small proportion. The flow top, with breccias and scoriaceous basalt in characteristic irregular lumps, reaches 2.5 m, bearing cavities that can exceed 30% of the total volume (Figures 6 and 7). It also includes breccias of amygdaloidal basalt clasts with stilbite-cemented crusts, in "Ouro Preto" mine. The scoriaceous top determines the surface limiting the use of material for crushing rocks on mine floors, which extract rocks from the overlapping acidic flow.



Figure 6. Scoriaceous zeolite-bearing basalt block removed from the mine floor of “Bairro Fátima”, with stilbite crusts.



Figura 7. Detail of cavities filled with heulandite, mordenite and fibrous zeolite with the appearance of cotton wool. Bairro Fátima mine.



Western Border Block

This is the block of land of the “Serra Geral Fácies Alegrete” formation, located west of “Jaguari-Mata” fault system. In this block, the breccias from the andesitic basalt flow tops *Catalán* (‘a’a) and *Cordillera* (pahoe) stand out, the 2nd and 3rd flows respectively of “Fácies Alegrete” (Hartmann et al. 2010). These flows are correlated to the other two flows that produced amethyst in large geodes in “Distrito Mineiro de Artigas” (DMA) in Uruguay.

In the *Catalán* flow top there are parageneses of **heulandite, calcite, hyalite and clay minerals, with subordinate stilbite and stellerite**. The best exhibits are located on “Santana do Livramento-Quaraí” highway, and breccias were also observed in the holes dug out for deployment of wind generators in the parks of “Cerro Chato” II and III, at the time of its opening, remaining as scattered material close to the towers.

In the *Cordillera* pahoe flow, there are **heulandite, scolecite and calcite** that can be the locally predominant phase, and subordinate **mordenite**.

Duarte (2008) cites the zeolites, heulandite and clinoptilolite among minerals of hydrothermal alteration in the flows that produce these in DMA. The lateral continuity of the *Catalán* and *Cordillera* flow top breccias in this block is remarkable, and they are followed in the field by indicators such as relief breaks in the slopes along tens of km².

On hilltops, they prove to be resistant to weathering, as in “Domo do Garupá” (Lisboa 1990) in Quaraí, where the breccia of the *Cordillera* flow top shows abundant optical calcite cementing amygdaloidal basalt clasts and in stockwork veins. In this location, the breccia thickness exceeds 7 m, and the amount of calcite using a visual estimate is over 20% in volume (Figure 8).



Figure 8. Breccia of the *Cordillera* flow top in Domo do Garupá. All the light material in the ground of the outcropping is optical calcite.

Conclusions

Brazil currently uses imported zeolites from Cuba (clinoptilolite) in agronomic trials, which aim to reduce the nitrogen losses. In contrast to the “pure” zeolites imported for this purpose, the mixture of zeolites observed in the amygdaloidal basalts has potential to adsorb different chemical elements and/or molecules, including NH_4 , K, Ca and Mg, which are often lost by the soil system. In addition, the presence of basalt matrix, rich in devitrified materials, can transport macro and micronutrients (P, Ca, Mg, Cu, Zn) to agricultural crops. Zeolite-bearing amygdaloidal basalt samples are in a testing phase in order to determine the possibility for its agronomic use, which can represent a positive impact in reducing the costs of agricultural production, as well as increasing the efficiency of fertilizers, especially nitrogen, which is usually very inefficient. The calcite-bearing breccias should also be submitted to agronomic tests in order to investigate their use for acidity correction in soils.



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