Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Zeolites of the Modern and Paleo-Hydrothermal Systems on Kamchatka

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Keywords: zeolites, physicochemical conditions, epithermal deposit, gold

ABSTRACT

Zeolites are indicator minerals for physicochemical conditions of hydrothermal and epithermal environment. Specific kinds of zeolites can be deposited only at certain temperature, pressure, and pH conditions. In general, hydrothermal zeolites deposit from saturated alkaline solutions within a wide temperature range and under low-pressure conditions. Zeolites are characterized by high absorbing ability, which may promote concentration of gold. Knowledge of zeolite typomorphic features could be used for more detailed and correct classification of geothermal and epithermal Au-bearing deposits. This is particularly important for estimation of potential of these materials, revealing their vicissitude, facial zonality, erosional shearing depth in detection of “blind” (hidden) ore bodies and geothermal reservoirs. However, because of their high absorption potential, zeolites complicate the ore processing. Zeolites have a neutralizing effect on the special reagents required for gold extraction processes. Zeolite minerals such as mordenite, heulandite, laumontite, and wairakite were identified in the high-temperature geothermal systems of Kamchatka. Scolecitee, barerrite, mordenite and laumontite are common minerals in the altered host rocks, and in metasomatic and gold-bearing quartz-adularia-carbonate epithermal veins. The presence of mordenite and laumontite in gold-bearing ores indicate the genetic similarity of the Kamchtkan extinct epithermal systems with the modern ones. Scolecitee and barerrite are typical of more complicated conditions at the near-surface deposition of gold and silver ores.

1. INTRODUCTION

Zeolite is a large group of minerals with similar composition. They are hydrous aluminosilicates with cations of potassium, sodium, calcium, and magnesium. Zeolites have been known as mineral species for over 200 years. For a long time they were considered as rare minerals, which do not form industrial clusters and interested only for collection purposes (Eremin). Zeololities are common minerals for the epithermal deposits in volcanic and islands arcs of the Pacific region.

General formula of a zeolite is:

$$Mm / n [(AlO_2) x (SiO_2) y] * zH_2O,$$

where x + y is the amount of tetrahedra per unit cell, m is the number of cation M, and n is the valence cation.

About 80 zeolite minerals of hydrothermal, exogenous, and metamorphic origin are known. They generally occur as infillings in fissures, cavities, pores in the volcanic and metasomatic rocks, and in schists and gneisses.

Typically zeolites are inhomogeneous in composition. Chemical compositions of zeolites vary widely. Some solid solutions are known. The crystalline structure of zeolites consists of tetrahedrons of $[SiO_4]_4$ - and $[AlO_4]_5$ - connected vertices openwork frames, cavities and channels, which are composed of metal cations, and H_2O molecule.

Zeolites are commonly used as an indicator of the physicochemical conditions of the hydrothermal and epithermal environment. Specific zeolite minerals form at certain temperature, pressure and pH conditions. Zeolites are minerals with high absorption potential, and they may contribute to the concentration of gold.

Knowledge of the typomorphic characteristics of zeolites can be used for more detailed and correct classification of geothermal and epithermal Au-bearing deposits. This is highly important for the economic significance of the precious metal deposits, their variability, erosion in way to find blind ore bodies and geothermal reservoirs.

Zeolites are broadly applied in the industry and in agriculture. They are used in the petrochemicals industry as a gas dryer, as media for the purification of drinking and industrial waters, for extraction of radionuclides, as catalyst, in construction, to improve the soil as fertilizer, to feed animals, and etc. If the zeolites completely remove adsorbed water in their cavities, they act as molecular sieves: a liberated cavities can selectively adsorb molecules of carbon dioxide, ammonia and other substances. Therefore, zeolites are used as adsorbents in chromatography, and also in cleaning, drying, and separation of gases.

World’s 1000 large zeolite deposits are located in more than 40 countries, including Russia. About 20 zeolite deposits are located in the Kuzbass region, and in Yakutia, Buryatia, Primorye, Kamchatka, and Sakhalin. This study investigates zeolites found in the epithermal and geothermal deposits of Kamchatka.

2. MODERN AND PALEO-HYDROTHERMAL SYSTEMS OF KAMCHATKA

Zeolites have been identified in the Mutnovsky high-temperature geothermal system (a modern hydrothermal system) as well as in the extinct hydrothermal systems of Asachinsky, Mutnovsky, Rodnikovy, Baranievsky, and Aginsky. Locations of the study areas are shown in **Figure 1**.

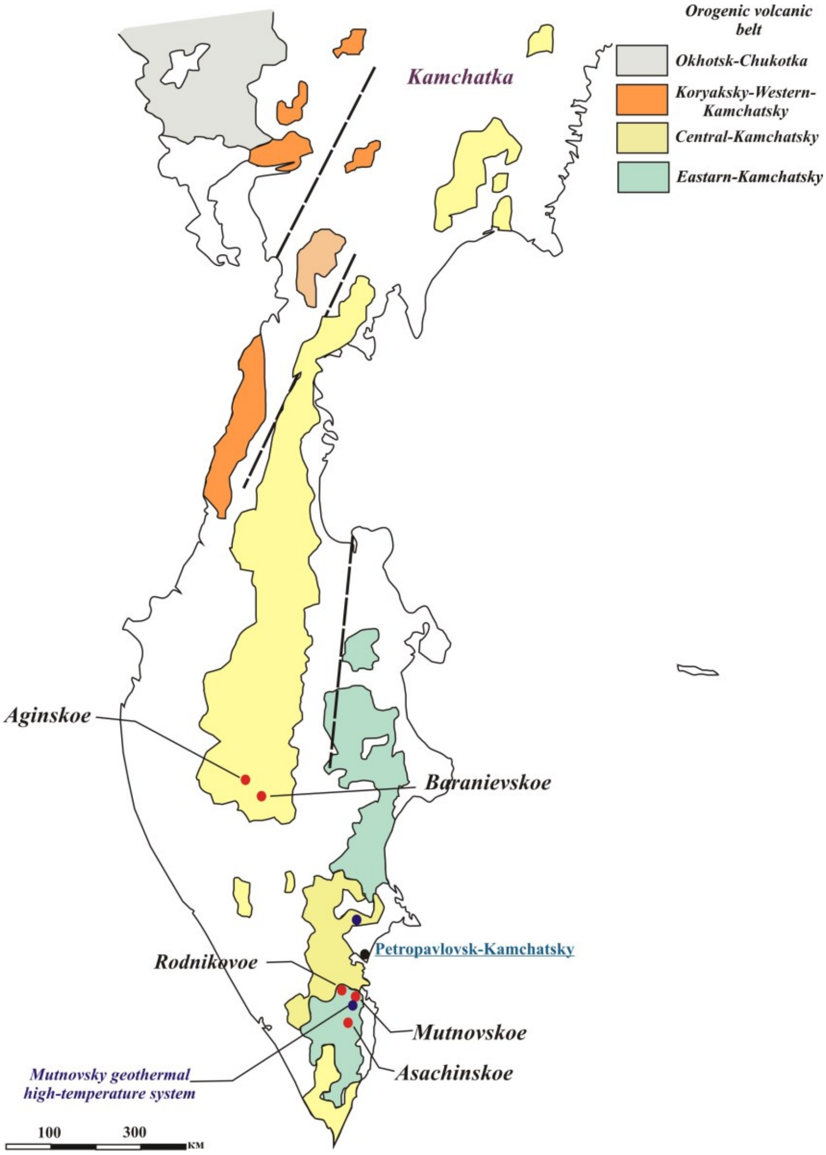

Figure 1: Locations of modern and extinct hydrothermal systems in Kamchatka.

2.1 Modern hydrothermal systems

2.1.1 Mutnovsky geothermal high-temperature system

The Mutnovskaya hydrothermal system is one of the most powerful and productive geothermal systems in terms of energy and heat production in the Kuril-Kamchatka island arc and in the northwestern area of a continent-ocean transition zone. It is located about 70–75 km southeast of Petropavlovsk-Kamchatsky city, on a volcanic plateau with elevations of 700–900 m a.s.l., in the Eastern Kamchatka volcanic belt (**Fig. 1**). The Mutnovskaya hydrothermal system is structurally related to the long-lived Mutnovsko-Asachinskoye volcanic center (Okrugin, 2006; **Fig. 1, 2**). Various epithermal precious metal and base metal deposits, geothermal deposits, and hydrothermal springs occurred nearby the Mutnovsko-Asachinskoye volcanic center. The Mutnovskaya hydrothermal system consists of two main productive zones: the Mutnovskiy deposit steam-hydrotherms and two geothermal power plants (Pilot Upper Mutnovskaya, 12mW and the Main power module, 50 mW), which provide up to 25–30% of the electricity supply for Petropavlovsk-Elizovo urban agglomeration. New wells are being drilled due to growing needs of the geothermal complex (**Fig. 2**). Modern drilling technology and operations provide information on the composition of the coolant (geothermal fluid) and the structure of the hydrothermal alteration haloes in a wide range of depths (up to 1,500 m), temperatures (up to 245°C), and pressures (greater than 45 atm).

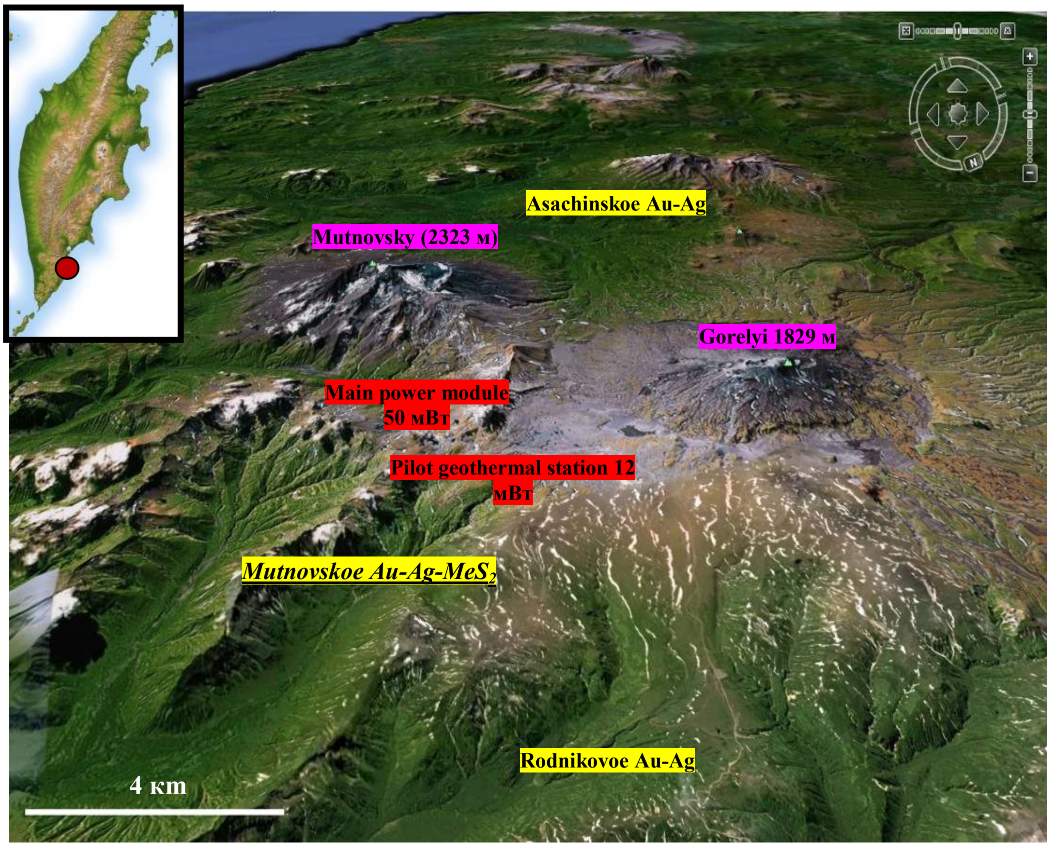

Figure 2: Satellite image showing the Mutnovsko-Asachinskoye volcanic center with locations of the studied deposits.

2.2 Paleo-hydrothermal systems (epithermal deposits)

Paleo-hydrothermal systems are analogous to modern hydrothermal systems, but they were formed in the geological past. Epithermal deposits are representative examples of the paleo-hydrothermal systems that widely occur in the volcanic belts of Kamchatka.

2.2.1 Asachinskoe epithermal deposit

The Asachinskoe Au-Ag deposit is a typical low-sulfidation epithermal deposit in South Kamchatka (**Fig. 1, 2**). It is located in the overlapping area between the South Kamchatka Pleistocene–Quaternary volcanic belt and the Central Kamchatka Oligocene–Pleistocene volcanic belt. The Asachinskoe deposit consists of more than 30 gold-bearing quartz veins, vein groups, and quartz veinlets. Vein zone 1 hosts majority of the gold reserves (Borovikov et al., 2009).

Ore deposits of Asachinskoe are characterized by veined texture and breeding caused by varying ratios of quartz, carbonate, adularia, and ore minerals.

Quartz-carbonate-adularia veins are showing spectacular colloform-banded, cockade, streaky, mesh, and net structures. The abundance of breccias and brecciated textures increases with depth in combination with streaky, banded, and colloform deposits. Ore minerals are irregularly distributed within colloform-banded and brecciated ores.

2.2.2 Rodnikovoe epithermal deposit

The Rodnikovoye epithermal gold-silver deposit is one of the most well-studied sites of the Rodnikovoee ore field in Southern Kamchatka. It is located about 8 km to the north of the Asachinskoe deposit. The total resources of the deposit are estimated to be 5.5 tonnes of gold and 67.8 tonnes of silver. Structurally, the deposit is confined to the junction zone of the southern sector of Central and Eastern Kamchatka volcanic belts with Malko and Paul area transverse fault-block dislocations (**Figs. 1, 2**).

Ore deposits are represented by quartz-carbonate-adularia veins. Ore minerals comprise 3–5% of the veins. Nevertheless, there are some small nests and lenses in the veins, in which concentrations of sulfides and sulfosalts reach up to 10–25%. The distribution of gold and silver ores is extremely uneven. Coefficient of variation of gold varies from 130 to 150. Gold contents are between 0.1 and 130–140 g/t (with several bonanza grades of ~300–1200 g/t) and average at 2.5–30.5 g/t Au. The average ratio of gold to silver is 1:10. Silver concentration varies from 1.2 to 300–700 g/t with an average of 150–200 g/t. Ore textures are banded, colloform and crustiform-banded, massive, and brecciated (Okrugin et al., 2006).

2.2.3 Mutnovskoe epithermal deposit

Gold-silver-polymetallic ore deposits in this prospective complex are related to the Mutnovsky volcanogenic hydrothermal vein deposits, which have estimated resources of over 10 tonnes of gold and up to 5–10 tonnes of silver. The deposit is located in the southern part of the Kamchatka Peninsula, in the middle reaches of rivers and near the active Mutnovskiy and Gorelyi volcanoes (**Fig. 1,2**).

The ores are characterized by a combination of massive breccias, colloform-banded, crustiform-banded, streaky, and densely disseminated to nest-disseminated textures. Breccias with colloform bands are the most common textures (Mozzherina et al., 2012).

2.2.4 Aginskoe epithermal deposit

The Aginskoe epithermal deposit is located in the central part of the Kamchatka peninsula, about 20 km southeast of the Ichinsky active volcano. It is included in the group of gold-silver lode deposits of the Abdrahimovskoe ore field situated on the eastern flank of the Aginskaya caldera. This is one of the many Miocene to Pleistocene volcanoes of the Central Kamchatka Volcanic Belt, extending throughout the peninsula. The Kamgold Company began commercial exploration of the lodes in 2005. The total mined and unmined resources are estimated at approximately 39 tonnes of gold and 20 tonnes of silver, with an average grade of 38.6 g/t Au. The Au/Ag ratio is 7:1.

Geology of the mining area is mainly composed of Miocene volcanic rocks of the Alneyskaya Formation and Quaternary basaltic and andesitic lavas. The host rocks commonly vary from basaltic to andesitic compositions, and they locally consist of dacite. Fragments of the gabbro-diorite intrusions crop out in central part of the caldera (Petrenko, 1999).

Aginskoe shoot is predominantly composed of quartz, with minor adularia, calcite, and zeolite as rare gangue minerals. Although, we have recognized gold, altaite, and chalcopyrite as the main mineral species, minor hessite, sphalerite, and pyrite are also present with rare petzite. Previous studies reported on the wide distribution of various telluride minerals such as calaverite, krennerite, sylvanite, tellurium oxide and tellurium hydroxide, and tellurates (Liessman and Okrugin, 1994; Nekrasov, 1999). Galena and Se-bearing galena were also determined by earlier investigators as a minor but locally abundant mineral. Tellurium concentrations in the ore vary from 400 to 3498 ppm. The distribution patterns show a positive correlation with some important components such as gold, lead, and copper.

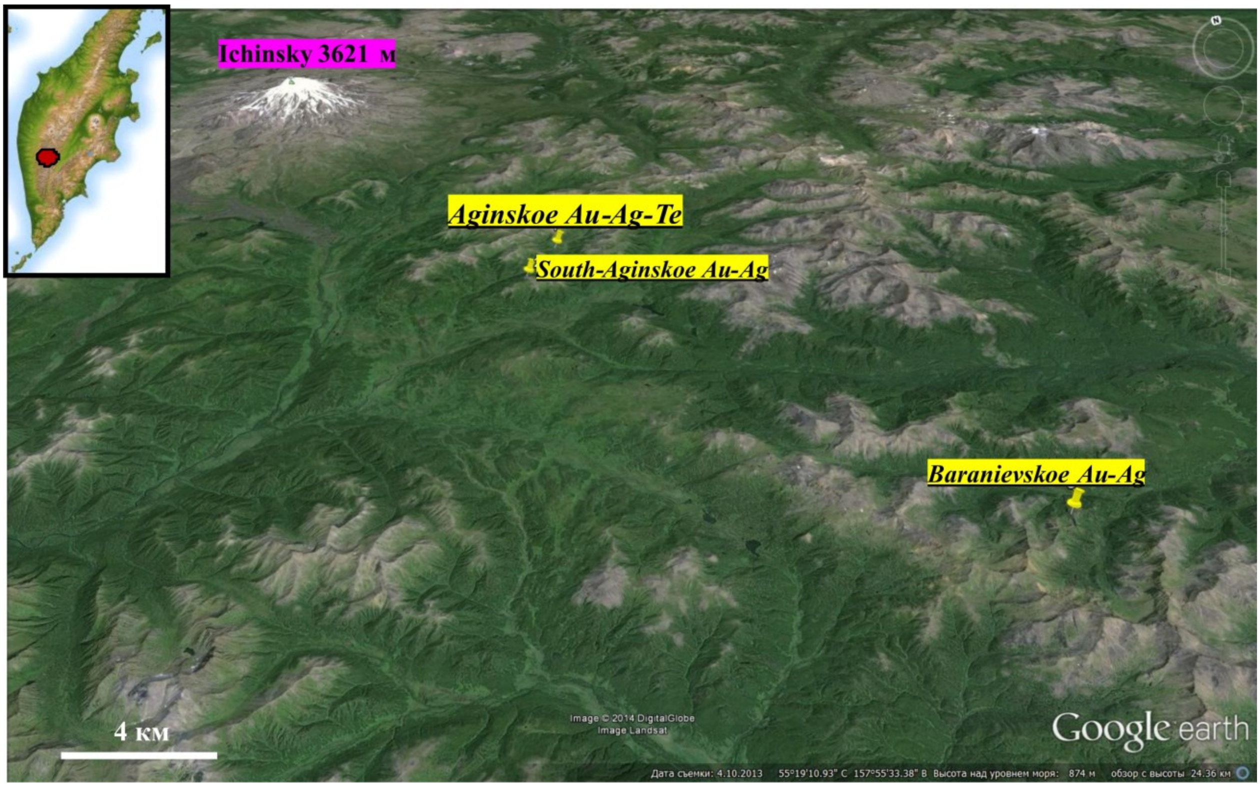

Figure 3: Central Kamchatka epithermal Au-Ag deposit.

2.2.5 Baranievskoe epithermal deposit

Baranyevskoe is an epithermal low-sulfide quartz vein-type gold deposit located within the Balkhach ore cluster. The Baranyevskoe deposit is situated in the southwestern part of the Central Kamchatka volcanic belt, approximately 400 km northwest of Petropavlovsk-Kamchatsky City and 70 km to the south of the Aginskoe deposit. Gold-ore cluster is confined to the Balkhach volcano-tectonic structure (VTS), which has a diameter of 22 km. Gold-bearing quartz orebodies are hosted in andesites and diorite porphyry of Late Miocene–Pliocene age. The proven resources of the Baranyevskoe deposit within an area smaller than 3 km^2 is 34.61 tonnes of gold (C1+C2), with an average grade of 9.2 g/t Au for the major gold quartz veins (Bolshakov et al., 2010).

The Baranevskoe deposit consists of three principally different ore types containing gold mineralization: quartz-adularia, copper, and carbonate ores. The former ore type is presented by veins fillings and stockworks of tiny veinlets in propylitized andesitic host rocks. Both veins and stockworks are characterized by abundant gold in association with sphalerite, galena, pyrite, and chalcopyrite, as is typical for low-sulfidation condition. Copper ore also hosts some gold, but the main ore mineral assemblage is chalcopyrite in contact with pyrite, bornite, falhore, and Cd-bearing sphalerite indicating intermediate to high sulfidation states. The last ore type is carbonate confined to the upper horizons of the epithermal system, which also contains some gold.

3 ZEOLITES OF MODERN AND PALEO-HYDROTHERMAL SYSTEMS

3.1 Zeolites of modern system

There are 22 Ca-montmorillonite group minerals and zeolites (ptilolit, natrolite, analcime, rare caporcianite), replacing up to 50% of the rock volume in the montmorillonite-zeolite zone of the Mutnovsky high-temperature geothermal system.

3.2 Zeolites of paleo-hydrothermal systems.

Paleo-hydrothermal systems	Zeolites
Asachinskoe	mordenite, scolecite, barerrite, laumontite
Mutnovskoe	scolecite, barerrite, mordenite, laumontite
Rodnikovoe	scolecite, barerrite, mordenite, laumontite
Baranyevskoe	laumontite, scolecite, mordenite, barerrite
Aginskoe	barerrite, scolecite, mordenite, laumontite
South- Aginskoe	chabasite

There are nine main mineralized quartz-vein zones and quartz veinlets in the Baranyevskoye field. The ore bodies are characterized by an elongated ribbon-like, less lenticular shape. The amount of quartz, adularia, and ore minerals increase with depth. In the upper horizons minerals such as arbonate, chalcedony, hydromica, clay minerals, and zeolites (barerrite) are present. Caporcianite was identified in the host rocks (**Fig. 4c**).

Zeolites of the Asachinskoe deposit are found in the ores and in the host rocks (**Fig. 4d**). They occur in aphyric andesites forming close intergrowths with quartz and adularia in vein quartz. Three groups of zeolites were identified confidently.

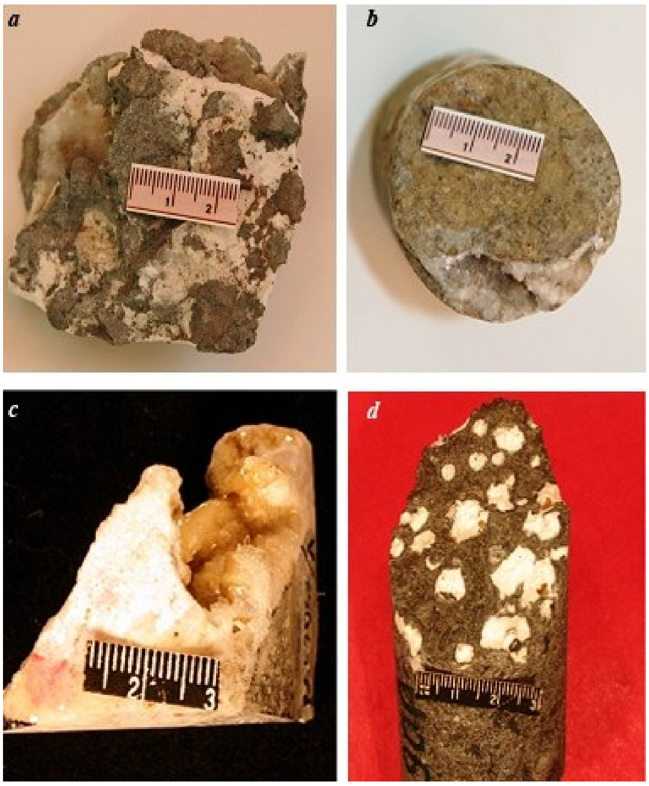

Figure 4: Morphology of zeolites: Aginskoe (a,b), Baranievskoe (c), Asachinskoe (d).

Barerrite ((Na$_2$, K, Ca) (Al$_8$Si$_{28}$) O$_{72}$*26H$_2$O) is one of the rare zeolite minerals. It was first found in the Rocky Pesse on Kuyu (Kuiu) Island in Alaska. Barerrite have been identified in the Aginskoe, Baranyevskoe, and Asachinskoe deposits. Trace elements are represented by Fe, Mn, Mg, Sr, and Ba. The morphology of barerrite from the Aginskoe deposit is shown in **Figure 4.** Electron microprobe analysis of this mineral indicated discontinuity in chemical composition.

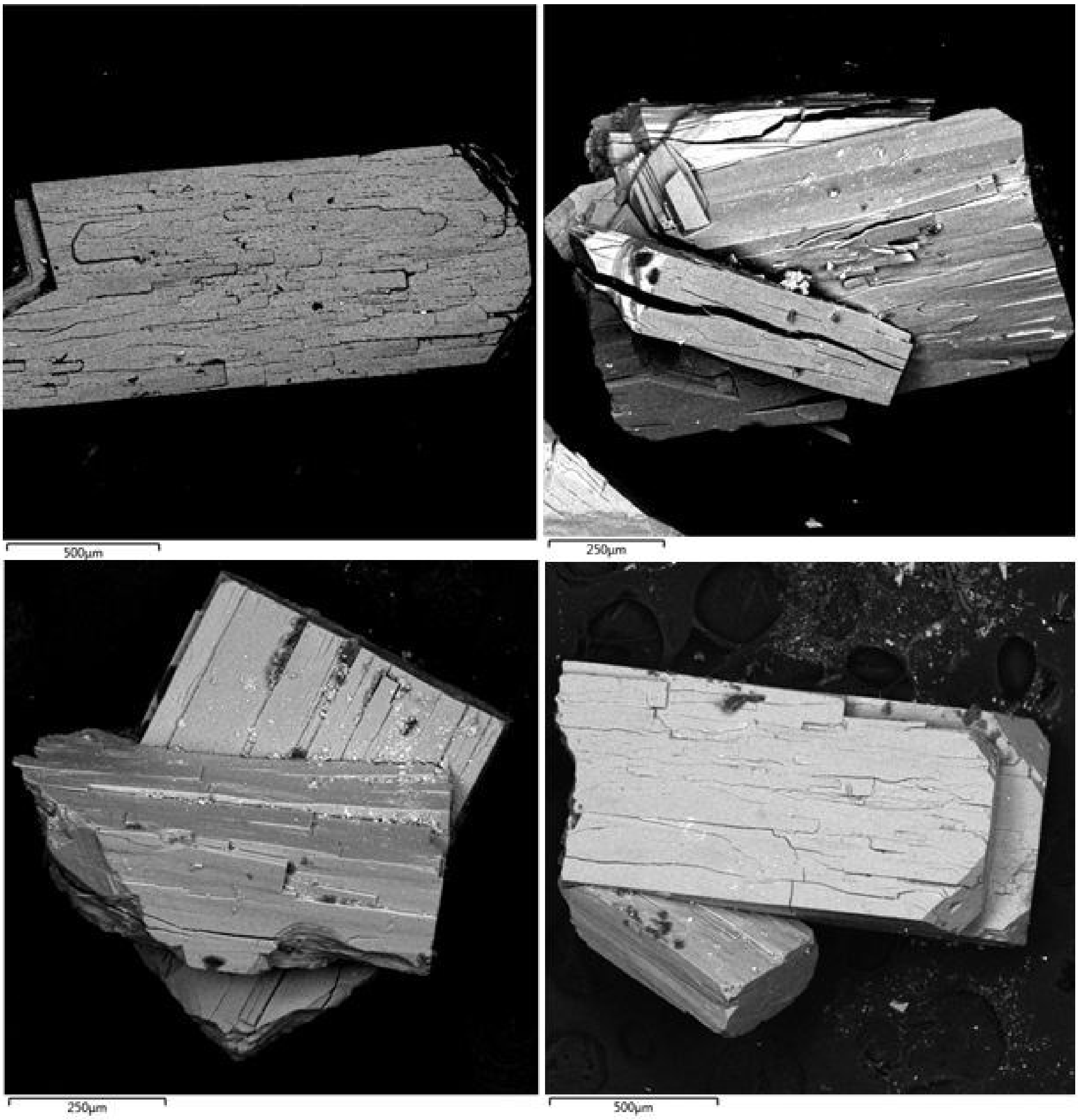

Figure 4: Crystals of barerrite, SEM.

Chabazite is a tectosilicate mineral of the zeolite group, and it is closely related to gmelinite with the formula (Ca,Na2,K2,Mg)Al2Si4O12·6H2O. Recognized varieties include Chabazite-Ca, Chabazite-K, Chabazite-Na, and Chabazite-Sr, depending on the abundance of the indicated cation. Chabazite crystallizes in the triclinic crystal system with typically pseudocubic rhombohedral crystals. The crystals are typically twinned, and both contact twinning and penetration twinning were observed. Small amounts of impurities contain Ba. Chabazite was identified by authors in the South-Aginskoe epithermal deposit **(Fig. 6, 7).**

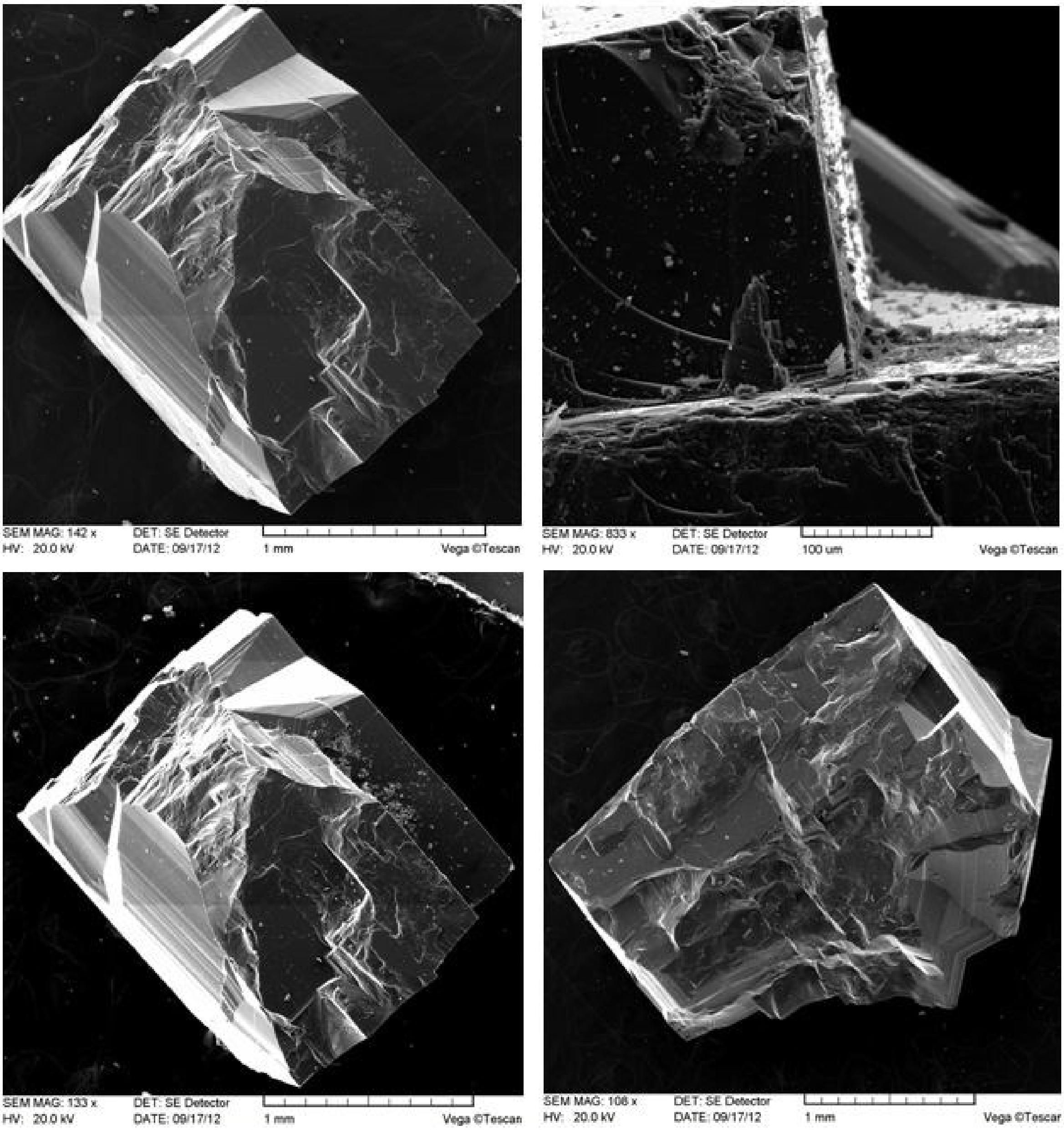

Figure 7: Morphology of crystals of chabasite, SEM.

Knowledge of typomorphic features of epithermal ores, hydrothermal alteration and geothermal deposits, as well as deposits of the modern hydrothermal systems expands our understanding of the relationship between volcanism and mineralization, and plays an important role in assessing the prospects of new territories.

ACKNOWLEDGMENTS

This work was carried out with financial support from the Strategic Development Program of Vitus Bering State University (2012-2014 years) and Far-Eastern Division of the Russian Academy of Science.

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