

# Transformations of Components Investigated Using Multimethodical Approaches

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## Abstract

The isomorphism of S-bearing feldspathoids belonging to the cancrinite, sodalite, tugtupite, vladimirivanovite, bystrite, marinellite and scapolite structure types has been investigated using a multimethodical approach based on infrared, Raman and electron spin resonance (ESR), as well as ultraviolet, visible and near infrared (UV-Vis-near IR) absorption spectroscopy methods and involving chemical and X-ray diffraction data. Sapozhnikovite  $\text{Na}_3(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{HS})_2$  and sulfite and thiosulfate analogues of cancrinite are synthesized hydrothermally and characterized by means of electron microprobe analyses, powder X-ray diffraction and Raman spectroscopy. The possibility of the incorporation of significant amounts of  $\text{SO}_4^{2-}$ ,  $\text{S}_4$  and  $\text{SO}_3^{2-}$  in the crystal structures of cancrinitite, sulfhydrylbystrite and marinellite, respectively, has been established for the first time. Thermal conversions of S-bearing groups in the synthetic sulfite cancrinite and sapozhnikovite analogues as well as natural vladimirivanovite and  $\text{S}_4$ -bearing hauyne under oxidizing and reducing conditions have been studied using the multimethodical approach. The  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  anions and the  $\text{S}_3^-$  radical anion are the most stable S-bearing species under high-temperature conditions (in the range of 700–800°C); their ratio in the heated samples is determined by the redox conditions and charge-balance requirement. The  $\text{HS}^-$  and  $\text{S}_5^{2-}$  anions are stable only under highly reducing conditions.

**Keywords:** Feldspathoids • Isomorphism • Solid solutions • Sulfur

## Introduction

A multimethod approach utilizing chemical and X-ray diffraction data, in addition to infrared, Raman, electron spin resonance (ESR), ultraviolet, visible and near infrared (UV-Vis-near IR) absorption spectroscopy, has been used to investigate the isomorphism of S-bearing feldspathoids belonging to the cancrinite, sodalite, tugtupite, vladimirivanovite. Hydrothermally produced sulfite and thiosulfate analogues of cancrinite, as well as sapozhnikovite  $\text{Na}_3(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{HS})_2$ , are characterized by powder X-ray diffraction, Raman spectroscopy and electron microprobe analyses. For the first time, the crystal structures of cancrinitite, sulfhydrylbystrite and marinellite have been shown to contain significant amounts of  $\text{SO}_4^{2-}$ ,  $\text{S}_4$  and  $\text{SO}_3^{2-}$ , respectively. The multimethodical approach was used to investigate the oxidizing and reducing thermal conversions of S-bearing groups in natural vladimirivanovite and  $\text{S}_4$ -bearing hauyne as well as synthetic sulfite cancrinite and its analogues. Under high temperatures (between 700 and 800°C), the most stable S-bearing species are the  $\text{SO}_4^{2-}$ ,  $\text{S}_2$  and  $\text{S}_3^-$  radical anions. The charge-balance requirement and redox conditions determine their proportion in heated samples. Only in highly reducing conditions are the  $\text{HS}^-$  and  $\text{S}_5^{2-}$  anions stable.

Feldspathoids are framework aluminosilicates (tectosilicates) with extra-framework anions (microporous aluminosilicates from the sodalite, cancrinite and scapolite groups) or are anhydrous (leucite and nepheline-group minerals). Feldspathoids' extra-framework components serve as important indicators of redox conditions and volatile component fugacities during rock formation. However, the microporous compounds of topological sodalite and, to a lesser

extent, cancrinite are regarded as advanced materials that can be utilized in a variety of technologies. S-bearing species are the most diverse, as shown by the above list of extra-framework components found in feldspathoids: S-bearing species in feldspathoids have oxidation degrees ranging from 0 to 6, polymerization degrees ranging from 1 to 6 and charges ranging from 0 to 2. The study of various sulfur forms and the mechanisms underlying their mutual transformations has established a theoretical and methodological foundation to date. In this paper, we give new information on the development, isomorphism and common changes of S-bearing extra-structure parts in some feldspathoids and their engineered partners [1,2].

## Description

According to the crystal structures of S-bearing feldspathoids, only species with an n 5 can exist in sodalite cages among the acyclic polysulfide groups  $\text{Sn}$ ,  $\text{Sn}_2$  and  $\text{Sn}^-$ . Slyudyankaite, a mineral with a sodalite framework topology, has a cyclic  $\text{S}_6$  molecule, which causes the symmetry of the  $\text{S}_6^-$  and  $\text{SO}_4^{2-}$ -bearing sodalite cages to shift frequently and triclinically. Only the Losod cages of minerals in the bystrite-sulfhydrylbystrite solid-solution series contain the acyclic  $\text{S}_5^{2-}$  anion, which is typically present in variable amounts. Aside from bystrite-type minerals, the  $\text{HS}^-$  anion is known in sapozhnikovite and the results of the warming of other S-bearing sodalite-bunch minerals under unequivocally decreasing circumstances (over the Fe-FeS cradle). These facts, along with the fact that sapozhnikovite is found in close proximity to the oxalate member of the cancrinite group kianoxalite, lead one to believe that the  $\text{HS}^-$  and  $\text{S}_5^{2-}$  anions are indicators of extremely reducing conditions. The sulfite analogues of cancrinite-group minerals, such as the  $\text{SO}_3^{2-}$ -bearing analogue of marinellite described in this paper and sulfite minerals with the afghanite-type framework described elsewhere, are formed under moderately reducing conditions [3-5].

These minerals have structural relationships with sodalite-group minerals. These data demonstrate that minerals with the lowest sulfide sulfur content (1.4 wt.%) and highest sulfide sulfur content (>4 wt.%) are cubic, whereas minerals with intermediate sulfide sulfur content have a lower symmetry. A sodalite-group mineral with high concentrations of sulfate anion, trisulfide radical anion, or cyclic hexasulfide molecule exhibits a commensurate or incommensurate modulation of the crystal structure, which may be caused by differences in the sizes of sodalite cages housing large  $\text{SO}_4^{2-}$ ,  $\text{S}_3^-$ , or  $\text{S}_6$  groups. Except for sapozhnikovite, the structures of all S-bearing minerals with

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a framework topology similar to that of a sodalite contain significant amounts of these groups.

In order to obtain the framework aluminosilicates with incorporated S-bearing anions, we utilized the conventional process of geopolymer production, which involves an aluminosilicate precursor and a soluble alkaline medium, preferably Na or K hydroxide solutions. All syntheses of sodalite- and cancrinite-type compounds were carried out under mild hydrothermal conditions at temperatures ranging from 180°C to 230°C within 16-24 hours. In addition, the crystallization conditions of sodalite- and cancrinite-group minerals in postmagmatic alkaline rocks are simulated by this approach. As an aluminosilicate source, a highly dispersed powder of metakaoline was used to create S-bearing sodalite-type phases. Powder X-ray diffraction was used to confirm metakaolinite's purity. In the trial with  $\text{Na}_2\text{S}_2\text{O}_3$ , 1.5 g of  $\text{CaCl}_2$  was added to the charge. The samples were cleaned with distilled water and dried in a cabinet dryer oven after the experiments were finished.

By heating initial powders in a muffle furnace at 700-800°C for 6 hours in uncoated crucibles in contact with atmospheric air (oxidizing conditions) and crucibles with carbon tablets (reducing conditions), the thermal transformations of S-bearing extra-framework anions in the synthesized materials under various redox conditions were investigated. Powder X-ray diffraction patterns were used to determine the cell parameters and space group assignments, taking into account the systematic absence of reflections. The structures of all the products' compounds are sodalite or cancrinite. The compound information for the manufactured stages are introduced. The oxygen equivalent of polysulfide groups could not be determined for the product of Experiment 1b, which contained both  $\text{SO}_4^{2-}$  and polysulfide groups in undetermined proportions (see below). Since all of the sulfur in this sample is reported as  $\text{SO}_3$ , the analytical total was high [6].

## Conclusion

To identify a variety of S-bearing extra-framework anions, radical anions and neutral molecules in feldspathoids belonging to the sodalite, cancrinite and scapolite groups, researchers used a multimethod approach that combined chemical and structural data with a variety of spectroscopic techniques. During high-temperature heating, these components undergo intricate mutual transformations. It was confirmed that the composition of an extra-framework

species in these minerals can be considered a marker of mineral-forming media, including the fugacities of the volatile components ( $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , HF,  $\text{SO}_2$  and polysulfide compounds), based on these data and data on the synthesis of S-bearing feldspathoids under reducing and oxidizing conditions. At high temperatures and in oxidizing conditions, the most stable species are the  $\text{SO}_4^{2-}$  and  $\text{S}_3^-$  radical anion.

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## Conflict Of Interest

None.

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