A NATROALUNITE – ZAHERITE – HOTSONITE PARAGENESIS FROM POFADDER, BUSHMANLAND, SOUTH AFRICA

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ABSTRACT

Large lenses of sillimanite occur in biotite-sillimanite schist 60 to 70 km west of Pofadder, South Africa, in the Wortel Formation of the Bushmanland Group. In one of the abandoned sillimanite quarries on the farms Hotson and Koenabib, the paragenesis sillimanite - natroalunite - zaherite - hotsonite was found. It is associated with silicates (kaolinite, pyrophyllite, topaz, muscovite and biotite), oxides (diaspore, rutile, ilmenite and corundum), sulfides (chalcopyrite, covellite and pyrite) and sulfide alteration products (covellite and goethite, atacamite and chalcanthite). The prevalent sequence of alteration is from sillimanite to natroalunite to zaherite to hotsonite, which is also the sequence of decreasing relative abundance, but sillimanite was directly transformed to zaherite wherever alkali elements were locally scanty. The necessary sulfate was apparently supplied during the oxidation of sulfides such as chalcopyrite and pyrite.

Keywords: natroalunite, zaherite, hotsonite, sillimanite, Pofadder, Namaqua mobile belt, Bushmanland Group, South Africa.

Sommaire

On observe de grosses lentilles de sillimanite dans les schistes à biotite et sillimanite de la formation de Wortel du groupe de Bushmanland, de 60 à 70 km à l'ouest de Pofadder, en Afrique du Sud. Dans une des carrières de sillimanite abandonnées, sur les fermes Hotson et Koenabib, on a reconnu la paragenèse sillimanite - natroalunite - zaherite - hotsonite. L'assemblage minéralogique est associé à des silicates (kaolinite, pyrophyllite, topaze, muscovite et biotite), oxydes (diaspore, rutile, ilménite et corindon), sulfures (chalcopyrite, covellite et pyrite) et minéraux d'altération des sulfures (covellite et goethite, atacamite et chalcanthite). L'ordre d'altération prédominant va de sillimanite à natroalunite à zaherite à hotsonite, ce qui correspond à leur abondance relative décroissante. Cependant, là où les alcalins se faisaient rares, la sillimanite se transformait directement en zaherite. L'oxydation de sulfures, tels que chalcopyrite et pyrite, semble avoir fourni le sulfate nécessaire aux transformations.

(Traduit par la Rédaction)

Mots-clés: natroalunite, zaherite, hotsonite, sillimanite, Pofadder, ceinture mobile de Namaqua, groupe de Bushmanland, Afrique du Sud.

INTRODUCTION

During the investigation of sillimanite-bearing rocks near the town of Pofadder in Bushmanland, South Africa (Fig. 1), an unusual aluminous mineral paragenesis was encountered. This includes the rare minerals hotsonite (Beukes *et al.* 1984b) and zaherite (Beukes *et al.* 1984a).

REGIONAL GEOLOGY

The area under consideration is situated in the Namaqua mobile belt. The relevant Proterozoic metamorphic rocks belong to the Bushmanland Group (Blignault 1980). The aluminous minerals occur in a biotite-sillimanite schist of the Wortel Formation (Praekelt et al. 1983). This formation also includes quartz-feldspar gneiss and quartzite. The Wortel Formation is bounded to the north by the Koeipoort granite (granitic gneiss) and to the south by a thrust contact with the Hotson Formation (Praekelt et al. 1983). In order to avoid confusion, the term Namies Schist (Formation), which was previously used for the rock unit under consideration (Joubert 1974, 1975, Rozendaal 1978), will not be used because it may be applicable to biotitesillimanite schists of different ages from both the Wortel and Hotson Formations.

Large pods and lenses of sillimanite, with a size range of a few metres to hundreds of metres along strike, occur in the biotite-sillimanite schist. The largest of these bodies were exploited until recently by means of small open-cast mines that are situated chiefly on the farm Hotson (portion of Wortel 42), and locally identified in a numbered sequence, from Hotson 1 to Hotson 7 (Fig. 2). The mineral paragenesis discussed in this paper was found in the Hotson 6 open cast on the farm Koenabib 43 (Fig. 3). Structurally, the sillimanite quarry under consideration is situated on the northern limb of the Haramoep antiform (Fig. 2).

MINERAL ASSOCIATIONS

Although much of the massive sillimanite has been removed during mining operations, veins of predominantly white alteration-products in sil-



FIG. 1. Locality map.

The alteration products, identified by optical microscopy and X-ray diffraction, include silicates, oxides, sulfates and sulfides. The prevalent silicates are kaolinite, pyrophyllite, topaz, muscovite and biotite. The oxides are diaspore, rutile, ilmenite and, rarely, corundum. Hydrated oxides are common, particularly goethite. The sulfides and sulfide alteration-products are chalcopyrite, pyrite, covellite, chalcanthite, atacamite and, rarely, brochantite. Sulfates are represented by natroalunite, zaherite and gypsum. This deposit represents the second major occurrence of zaherite (Beukes et al. 1984a). The zaherite is associated with a new hydrated aluminum phosphate-sulfate named hotsonite (Beukes et al. 1984b). Rare grains of the phosphate turquoise were also identified.

The evidence that the four minerals sillimanite, natroalunite, zaherite and hotsonite are genetically related is best presented in the form of photographs and photomicrographs. Replacement textures representing the alteration of sillimanite to natroalunite were observed in many hand-specimens and thin sections (Figs. 4a, b), but in a few instances sillimanite is in contact with zaherite (Figs. 4c, d). The replacement of natroalunite by zaherite is difficult to observe in thin section because of problems in sample preparation but is illustrated in many hand-specimens (Fig. 4h). The less prevalent transformation of zaherite to hotsonite is represented by several specimens (Figs. 4e, f, g).

MINERAL REACTIONS

The above petrographic and field evidence concerning the mineral association sillimanite – natroalunite – zaherite – hotsonite supports a petrogenetic model that involves four chemical reactions. Hotsonite was formed by a chain of reactions that sequentially entailed the transformation of sillimanite to natroalunite, natroalunite to zaherite and zaherite to hotsonite, which is also the order of relative abundance at the Hotson 6 quarry on the farm Koenabib. In a few instances zaherite has formed directly from sillimanite. The prevalent appearance of natroalunite as the first member of the reaction chain was apparently controlled by the local availability of abundant sodium. It should be noted that all the veins at Koenabib have natroalunite, never alunite, which contrasts with many other comparable occurrences (Bladh 1982, Brophy *et al.* 1962, Parker 1962, Slansky 1975, Cunningham & Hall 1976).

The first reaction of the series can be written:

$$3(Al_2O_3 \bullet SiO_2) + 2Na^+ + 4(SO_4)^{2^-} + 3H_2O + 6H^+$$

sillimanite
= Na_2O \bullet 3Al_2O_3 \bullet 4SO_3 \bullet 6H_2O + 3SiO_2
natroalunite

A source of sodium is close at hand in the feldspar of the country rock and its alteration products. It is known that potassium is preferentially incorporated with respect to sodium during alunitization (Parker 1962), suggesting that the sodium-topotassium ratio was very high in the acidic fluids (Höller 1967, de Abeledo *et al.* 1968) responsible for the mineral reactions at Koenabib. The possible source of sulfur will be discussed below.

Natroalunite can be transformed to zaherite by the reaction:

$$2(Na_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O) + 22H_2O =$$
natroalunite

$$6Al_2O_3 \cdot 5SO_3 \cdot 33H_2O + 4Na^+ + 3(SO_4)^{2^-} + 2H^+$$
.
zaherite

The transformation merely involves the removal of sodium and some of the sulfate in a hydrous medium. This could easily have been accomplished during a local hydrothermal or weathering event.

The direct reaction of sillimanite to zaherite consumes no sodium:

$$6(Al_2O_3 \cdot SiO_2) + 5(SO_4)^{2^-} + 28H_2O + 10H^+ =$$

sillimanite

$$6Al_2O_3 \cdot 5SO_3 \cdot 33H_2O + 6SiO_2$$

zaherite

It would seem that this transformation merely requires a very hydrous environment and a source of sulfate, but the fact that the transformation of sillimanite to natroalunite was much more common indicates that a local deficiency of alkalis must be essential as well. This is probably the reason for the relative rarity of zaherite.



FIG. 2. Simplified geological map of the farm Hotson, 65 km west of Pofadder. The numbers (1 to 7) indicate sillimanite quarries. Structurally, the metasedimentary formations, including an associated thrust-plane, define the Haramoep antiform in the north and a complimentary synform in the south.

limanite can be seen in the walls of the Hotson 6 and Hotson 7 mines. The veins vary in width from a few mm to ten cm (Figs. 4a, c).

The reaction responsible for hotsonite, the final event in the postulated chain of reactions, differs markedly from the preceding transformations: $11(6Al_2O_3 \cdot 5SO_3 \cdot 33H_2O) + 12P_2O_5 =$ zaherite $6(11Al_2O_3 \cdot 2P_2O_5 \cdot 6SO_3 \cdot 53H_2O)$ hotsonite $+ 19(SO_4)^{2^-} + 26H_2O + 38H^+.$



FIG. 3. Map of the sillimanite quarries known as Hotson 6 and Hotson 7, on the farm Koenabib. The respective maximum depths are 35 m and 8 m. The excavations are situated in the Wortel Formation of the Bushmanland Group.

This is the only reaction of the series that exhibits prograde characteristics, involving the removal of some of the sulfate and water. A small amount of the hotsonite could also have been formed together with natroalunite by more complex reactions involving both sillimanite and zaherite, but the evidence for this possibility is tenuous. The source of the phosphate essential for the formation of hotsonite is at present obscure.

The sulfate required for the formation of natroalunite, zaherite and hotsonite presents no problem because sulfides are ubiquitous in the country rocks as well as in the sillimanite ore. The fairly abundant chalcopyrite is extensively altered to covellite and goethite, and encrustations of chalcanthite and atacamite are common. From a volumetric viewpoint, the amount of sulfide-group minerals present could easily have produced enough sulfate to account for the alteration veins under discussion. Additional evidence that chalcopyrite was involved is supplied by the presence of light green cupriferous natroalunite in the thin border-zones of some alteration veins of white natroalunite (Beukes et al., in prep.). Some authors who have studied comparable deposits elsewhere have even proposed that the occurrence of alunite or natroalunite in the proper

environment can be used as an indicator of hidden sulfide mineralization (Kerr 1951, Sheridan & Royse 1970, Cunningham & Hall 1976). We are not suggesting that the deposit at Hotson 6 is indicative of a sulfide orebody, but the sulfate needed for the mineral reactions under consideration is derived from sulfides.

CONCLUSIONS

The hydrated sulfates of aluminum found on the farm Koenabib were formed by the hydration and sulfatization of sillimanite, with sulfate supplied by the oxidation of chalcopyrite and other sulfides. In local environments that were particularly low in alkalis, sillimanite was directly converted to zaherite, but in most instances natroalunite was formed rather than alunite owing to a high sodium-to-potassium ratio. The source of phosphate needed for the transformation of zaherite to hotsonite is unknown.

Abundant alunite and natroalunite are typical of the alteration of volcanic rocks, particularly those of felsic composition (Palache *et al.* 1951, King 1953, Ross *et al.* 1968, Sheridan & Royse 1970, Wise 1975, Cunningham & Hall 1976). As pyrophyllite is common in the deposit under consideration, note that



FIG. 4. Photographs (a, c, e, h), photomicrographs (b, d, f) and an electron micrograph (g) of alteration products (N natroalunite, Z zaherite, H hotsonite) of sillimanite (S) from the Hotson 6 quarry on the farm Koenabib. a, b. Replacement of sillimanite by natroalunite. c, d. Replacement of sillimanite by zaherite. e, f. g. Replacement of zaherite by hotsonite. Note acicular to lath-like microcrystals of hotsonite on curved flakes of zaherite (g). h. Replacement of natroalunite by zaherite.

a similar origin has been advanced for pyrophyllite parageneses (Zen 1961). However, alunitic deposits have also been ascribed to the alteration of granitic rocks (Bladh 1982, King 1953), sulfide veins in argillaceous schist (Moss 1958), and to sedimentary processes for volcanogenic material (Sheridan & Royse 1970).

The authors can present very little evidence that the precursor rocks of the sillimanite-enriched unit in the Wortel Formation were volcanic, or that they had been subjected to fumarolic activity. The mineral paragenesis discussed in this paper was formed by the hydration and sulfatization of sillimanite caused by some form of hydrothermal activity.

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