

Replacement of Nickelhexahydrite with Retgersite: Polymorphic–Metasomatic Structures

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Abstract—The polymorphous transition that occurs during the process of metasomatic replacement was observed in the experiment on the retgersite paramorph formation after nickelhexahydrite crystals. This process runs through a solution film formed on the primary crystal surface and then penetrated into the crystal along with the replacement front. One or several secondary mineral grains have ingrown into a comparatively perfect crystal up to the complete replacement; these grains are randomly oriented with regard to the crystal. A fine-grained mass replaces the imperfect crystals. An aggregate of mineral grains incorporated into the fine-grained mass is an intermediate case. Single-crystal pseudomorphs have been synthesized for the first time as products of the nonisomorphic interaction. Conditions of the nickelhexahydrite metastable equilibrium and the retgersite stable equilibrium are closely related and determine the structural features of the replacement reactions for these two compounds. A relatively low supersaturation with retgersite in the vicinity of the eutonic point resulted in the nucleation and growth of secondary single crystals. A deviation from the eutonic point gives rise to the increasing supersaturation and mass precipitation of the secondary phase.

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INTRODUCTION

Since the discovery of polymorphism by E. Mitscherlich (1822), numerous substances crystallized as different structure modifications have been described in data reports (Deffet, 1942; JCPDF, 1997), mineralogical reference books, and unnumbered articles. Modifications of carbon, iron disulfide, silica, calcium carbonate, and others are well known (Strunz and Nickel, 2001). The products of a polymorphic transition are characterized by a specific structure and can retain the outer shape of the initial crystal (paramorph). Features of these products provide evidence for the physicochemical environment during the formation of rocks.

A polymorphic transition is commonly considered as an immediate solid-phase transformation (Verma and Krishna, 1969; Anosov et al., 1976). These are paramorphs of low-temperature quartz after tridymite consisting of sporadic quartz grains, which are variously oriented with regard to the initial crystal. On the basis of these quartz grains, the host rocks are interpreted as heated and then rapidly cooled (Karpenko and Tantsseva, 1966). Paramorphs of graphite after a diamond presented by fine-grained structures with a complicated orientation are considered as evidence of an abrupt decompression within a hot ultramafic body (Slodkevich, 1981, 1987).

At the same time, the transition of one modification to another is possible by metasomatic replacement, i.e., due to the solution of an initial phase in a liquid and the

subsequent precipitation of a newly formed modification, e.g., α -LiIO₃ after β -LiIO₃ (Kidiyarov and Mitnitsky, 1977) or diamond after graphite (Chepurov et al., 1997). The results of an experiment on the replacement of nickelhexahydrite (β -NiSO₄ · 6H₂O) with retgersite (α -NiSO₄ · 6H₂O) and the relationships between paramorph structural features and phase equilibria are discussed in this article.

PHASE RELATIONS IN THE SYSTEM NiSO₄–H₂O

Within the temperature range 0–100°C, nickel sulfate forms a number of water-soluble crystalline hydrates that differ in the amount of water molecules in the formula, structure, and stability field. Structural data do not allow us to suggest the epitaxial parities between phases. *Retgersite* α -NiSO₄ · 6H₂O (Hurlbut and Klein, 1977; I-Ming Chou and Seal, 2003) pertains to the tetragonal–trapezohedral symmetry type 422, space group $P4_12_12$; the unit-cell dimensions are $a = 6.7801(1)$ and $c = 18.285(2)$ Å. The crystals are thick plates on {001} or short prismatic. The cleavage is perfect on {001}, with traces of cleavage on {110}. The mineral is brittle. Retgersite is dark emerald green with a light blue hue. *Nickelhexahydrite* β -NiSO₄ · 6H₂O (Winchell and Winchell, 1964) belongs to the rhombic–prismatic symmetry type $2/m$, space group $C2/c$; the unit-cell dimensions are $a = 9.88(3)$, $b = 7.228(2)$, $c = 24.130(3)$ Å, $\beta = 95.38(3)^\circ$. The crystals are basal plates. The cleavage is absent. The mineral is green. *Morenosite* NiSO₄ · 7H₂O (Winchell and Winchell,

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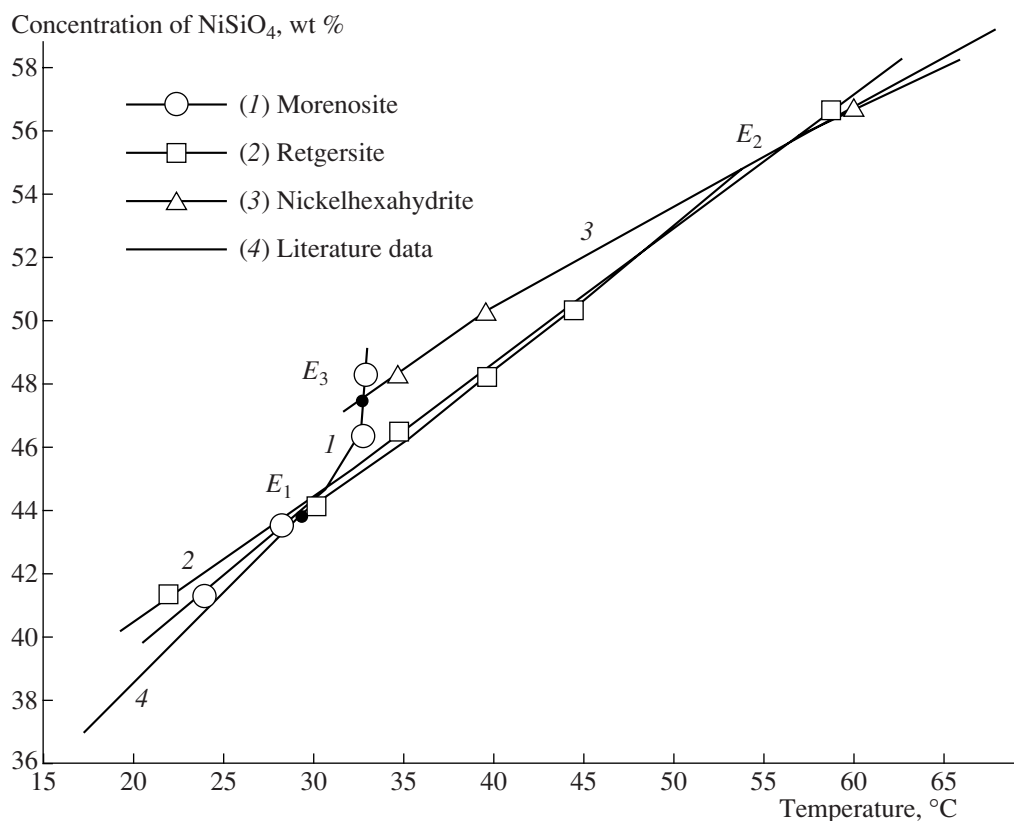


Fig. 1. Solubility of nickel sulfate in water and the stability fields of its crystalline hydrates: (1–3) our data; (4) after *Chemist's...* (1965).

1964) pertains to the rhombic-tetrahedral symmetry type; the unit-cell dimensions are $a = 11.8$, $b = 12.0$, $c = 6.80$ Å. The cleavage is perfect on {010}. The crystals are short-prismatic or fibrous. Morenosite is chartreuse in color.

Some of these phases, e.g., α - and β -modifications of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot \text{H}_2\text{O}$, occur in the oxidation zone of Ni deposits and are formed in water solutions containing sulfuric acid at pH 1.8–6.2 (Oleinikov et al., 1965).

In air, nickelhexahydrite ($\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$) is unstable and transforms into retgersite ($\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$) or $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ (Angel and Finger, 1988). Morenosite $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ transforms into retgersite with the formation of pseudomorphs (Pozin, 1974). The opposite replacement of retgersite by morenosite is observed at $\leq 31.1^\circ\text{C}$ in a water solution oversaturated with $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and undersaturated with $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$. Their simultaneous growth is observed at equal temperatures of saturation with both phases (Kukui, 1969). The crystallization of an unstable monoclinic polymorph $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was observed at 31.5°C as well (Hurlbut and Klein, 1977).

Phase relationships in the system $\text{NiSO}_4\text{--}(\text{H}_2\text{SO}_4)\text{--}\text{H}_2\text{O}$ have been studied for a long time (see the review in Soboleva et al. (1998)). Our experiments (Fig. 1) are consistent with the published data. Phase equilibria

were precisely determined with the microcrystallization method (Petrov et al., 1983). A seed was placed into a solution with a certain concentration. After that, indications of growth and dissolution at variable cycles of cooling and heating of the system with an approaching saturation temperature ($\pm 0.5^\circ\text{C}$) were recorded.

In acid-free solutions, the crystalline phases of morenosite, retgersite, and nickelhexahydrite are grouped into fields, which are divided by eutonic points E_1 and E_2 . Retgersite crystallizes within the range $31.5\text{--}53^\circ\text{C}$. Nickelhexahydrite crystallizes above 53°C , while morenosite, below 31.5°C . The metastable equilibria of retgersite beyond eutonic points E_1 (with morenosite) and E_2 (with nickelhexahydrite), as well as morenosite and nickelhexahydrite equilibria with their metastable eutonic point E_3 , are shown in Fig. 1.

It is extremely important that the solubility curve $\text{NiSO}_4\text{--}\text{H}_2\text{O}$ is close to the straight line with small kinks at eutonic points E_1 (morenosite–retgersite, approximately 30°C) and E_2 (retgersite–nickelhexahydrite, approximately 53°C). Metastable equilibria, here, turn out to be close to thermodynamic equilibria and, thus, may be traced in experiments at a distance from the eutonic points. As a result, we could observe the growth of morenosite crystals within the stability field of retgersite (from E_1 to 40°C), the growth of nickelhexahydrite in the stability field of retgersite (from E_2

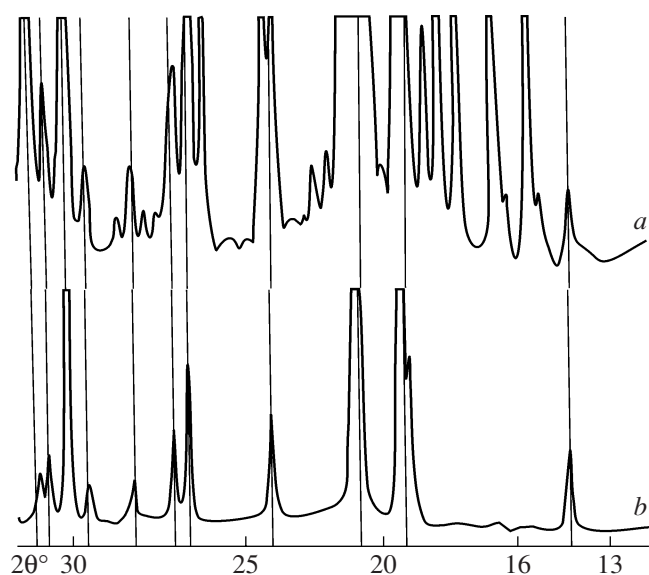


Fig. 2. Variation in the X-ray powder pattern of the sample on the transition of nickelhexahydrite to retgersite: (a) within 4 h after the preparation of the sample (mixture of phases); (b) within 24 h (monomineralic retgersite).

to 35°C), and the growth of retgersite in the stability fields of morenosite (from E_1 to 25°C) and nickelhexahydrite (from E_2 to 59°C).

It should be noted that the stability constraints of the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ polymorphs in acid solutions are not described in the literature. Our data confirmed that retgersite crystallizes under less acidic conditions than nickelhexahydrite (Hurlbut and Klein, 1977). The increase in the sulfuric acid concentration in a solution up to pH 3.5–4 and with a decrease in temperature are known to lower the solubility of NiSO_4 , so that the data points are displaced into the stability fields of crystalline hydrates of nickel sulfates with a lesser water content (seven water molecules $\rightarrow$ six water molecules $\rightarrow$

one water molecule). An increase in the sulfuric acid concentration is accompanied by a decreasing temperature of retgersite and nickelhexahydrite formation.

EXPERIMENTAL AND DISCUSSION

Crystals of monoclinic nickelhexahydrite 2 to 10 mm in size were synthesized from a water solution in the presence of sulfuric acid (pH $\sim$ 1) by a decrease in the temperature from 30 to 22–25°C. The crystals were removed from the solution and dried out with filter paper. Typical crystals are dominated by pinacoid {001} and rhombic prisms {111}, {011} and {101}, whereas pinacoid {100} and rhombic prisms $\{21\bar{1}\}$ and $\{31\bar{1}\}$ are developed poorly or partially. Parasitic crystals frequently form on the {001} pinacoid surface.

A phase transition of nickelhexahydrite to retgersite that starts immediately after crystal extraction from solution was visually detected from the changing color of the crystals from green to bluish green. A significant amount of retgersite is recorded in the X-ray powder diffraction pattern 4 h after preparation (Fig. 2a), and, in 24 h, nickelhexahydrite is completely replaced by retgersite (Fig. 2b). These phases were also identified with immersion method ($\alpha = 1.470$ and $\gamma = 1.493$ for nickelhexahydrite; $\omega = 1.510$ and $\epsilon = 1.484$ for retgersite, after Winchell and Winchell (1964)).

The outcropped opaque retgersite nuclei originate within the outer zone of the initial crystal after 10–15 min of paramorphous replacement. These nuclei were either faced single crystals randomly oriented to one another and in regard to the initial crystal (Fig. 3a) or fine-grained aggregates (Fig. 3b) related to imperfections in the initial crystal: areas of multiple-heading growth (Fig. 3b, 1), intergrowths with a parasitic crystal (Fig. 3b, 2), fractures, inclusions of growth solution, etc.

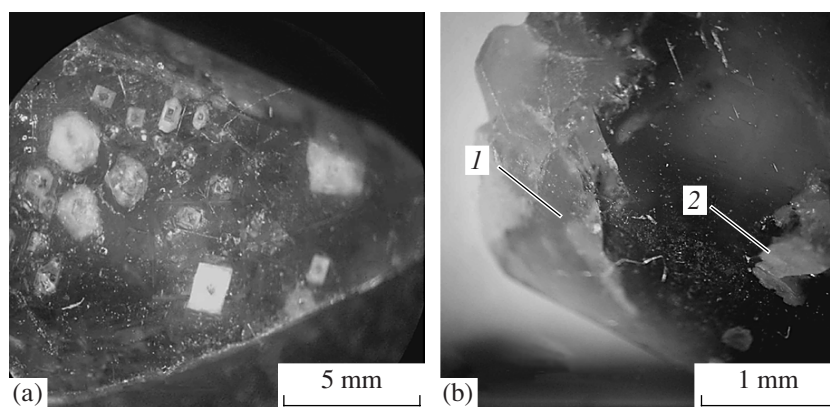


Fig. 3. Retgersite in the surface zone of a nickelhexahydrite crystal: (a) single crystals of retgersite (light) in nickelhexahydrite (dark); (b) segregation of retgersite in imperfect areas of nickelhexahydrite related to (1) a multiple-heading and (2) an overgrowing parasitic crystal.

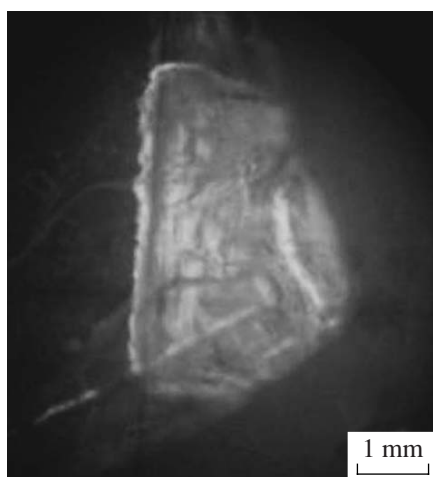


Fig. 4. Stresses (light band) in the nickelhexahydrite crystal (dark background) along the interface with the ingrown retgersite crystal (gray). Replacement option 1. Crossed polars.

The next stage resulting in the complete replacement of the initial crystal is represented by three variants that correspond to structurally distinct paramorphs.

(1) The framing of the initial mineral by a transparent material, which develops as a faced crystal ingrown into a primary crystal and completely replacing the latter. While the initial size is 1.5–2 cm, the replacement endures for about 5 days. In the case of a single replacing individual, a monocrystal is formed. Such a process is characteristic of transparent initial crystals without notable imperfections. In this case, strong stresses are detected at the interface under the crossed polars (Fig. 4). These stresses can relax in fractures deeply penetrating into the nickelhexahydrite crystal. As the growing crystal of retgersite devours the primary crystal, the fractures disappear. Stress can arise due to the replacement with an excess volume (Glikin, 2004), although, as follows from Fig. 1, the slopes of the equi-

librium isotherms of both phases differ insignificantly and, therefore, the volumetric effect is probably small.

(2) The crystallization of retgersite in the volume of the nickelhexahydrite crystal as an opaque bluish green fine-grained mass composed of fibrous–columnar and/or radiaxial aggregates (Fig. 5a). This pattern is extremely distinct, while the initial crystal has a great deal of defects (fractures, growth zones, splitting blocks). The duration of the complete replacement of the initial crystal 1.5 to 2 cm in size is about 24 h.

(3) The formation of a combined paramorph composed of large crystals incorporated into a fine-grained groundmass. First, the large retgersite crystals arise and grow such as that in option (1) (Figs. 3 and 4). Then, their growth sharply decelerates, and the relict part of nickelhexahydrite is gradually replaced with a fine-grained aggregate similar to variant (2) (Fig. 5b). While the size of the primary crystal ranges from 1.5 to 2 cm, the large crystals were growing over 1–1.5 days and the rest period of the replacement continued from 2 to 5 days.

The rate and character of the replacement strongly depend on the presence of the mother solutions or solutions on the basis of the water condensate formed in humid air on the surface of the initial crystal. The careful removal of the mother solutions from the crystal surface and the fairly high quality of the initial crystal provide a small number of retgersite nuclei and replacement develops in line with option (1). The worse the drying-out of the initial crystal after removal from the solution, the more nuclei are formed on its surface and, in the limit, the process develops according to option (2). This phenomenon suggests that the polymorphic transition is driven by metasomatic replacement through the solution, which, at the initial stage, occurs as a film on the surface of the primary crystal and subsequently percolates into the space between the replacing and replaced crystals. The formation of the fine-grained aggregate both in options (2) and (3) can be caused by the multiplication of fractures and other imperfections

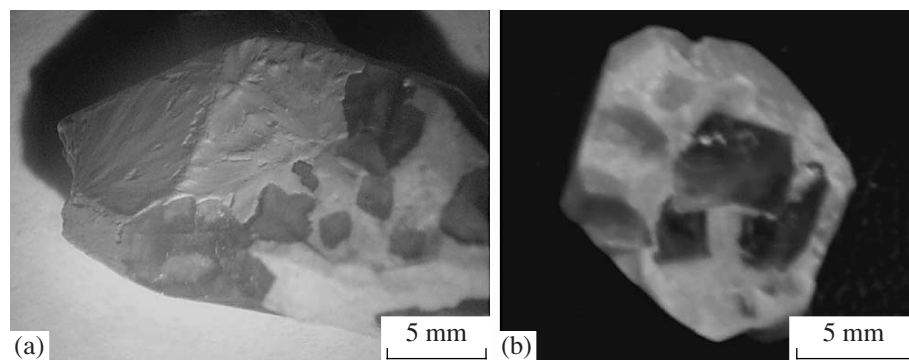


Fig. 5. Retgersite aggregates forming paramorphs after nickelhexahydrite: (a) volumetric fibrous-columnar (light gray) and superficial radiaxial (dark gray) fine-grained aggregates (replacement option 2); (b) combined coarse- and fine-grained aggregate (replacement option 3).

in the primary crystal due to the strain at the replacement front. The strain can be enhanced while the front is passing through the defect areas. In this case, inclusions within such areas serve as the sources of additional portions of the solution in the reaction zone that accelerate the replacement.

It should be noted that the transition from single-crystal to polycrystalline replacement during the formation of a combined paramorph (option 3) is accompanied by a deceleration of the process to a degree that does not correspond to the rates that are characteristic of options (1) and (2). It is premature to speculate about the replacement mechanism, because the combined variant was observed in rare cases and its kinetics remain ambiguous in contrast to the much more definite options (1) and (2).

Let us turn again to the phase diagram (Fig. 1). The suggested metasomatic mechanism of the polymorphic transition implies the dissolution of nickelhexahydrate and conjugate precipitation of retgersite. Such a process can be realized owing to a change in the solution temperature or the evaporation of the solvent, when a data point is situated between the line of metastable equilibrium of nickelhexahydrate and the line of stable equilibrium of retgersite. It is important that the oversaturation of the solution with retgersite must be relatively low in a wide range of conditions, because these lines are close to each other. Therefore, sporadic secondary crystals should nucleate and develop in the vicinity of eutonic point E_2 , and a certain increase in the concentration must give rise to the mass crystallization. This is the critical point in the interpretation of the observed structural relationships.¹ Similar phenomena may be suggested on replacing retgersite by nickelhexahydrate in the same system on the opposite side from the eutonic point, as well as in other systems of a similar type, for example, in the system α - LiIO_3 - β - LiIO_3 - H_2O that has closely adjoining lines of metastable and stable equilibria (Franke et al., 1981).

In conclusion, note that the previously suggested classification of replacement products limits the formation conditions of single-crystal pseudomorphs by reactions with specific mechanisms in continuous isomorphic series (Glikin and Sinai, 1983, 1991; Glikin, 2004). In this study, we managed to investigate the single-crystal replacement in the absence of an isomorphism between the primary and secondary phases. Natural products of this process have not yet been

described in the literature. A random orientation of the secondary crystal with regard to the faces of the initial crystal may be an indication of such products. In general, this phenomenon distorts the genetic distinctness in the classification of the replacement products and the replacement structures acquire convergent features.

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¹ The idea of a single-crystal pseudomorph formation under a slight oversaturation with a secondary phase was first stated by E.B. Treivus (personal communication). Therefore, Treivus launched pioneering experiments on the modeling of metasomatic replacement of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals in a solution of K_2SO_4 (unpublished BSc thesis by D.P. Sipovsky, 1962, archive of the Department of Crystallography, St. Petersburg State University; Treivus and Rozhnova, 1962). However, single-crystal pseudomorphs were not obtained.

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