Synthesis of the fluorine end member of the fluoborite series

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Abstract

The extent to which pressure and presence of water affect the crystallization temperature of the fluorine end member of the isomorphous fluoborite series was determined by synthesis experiments. The *a* parameter of synthetic fluoborite varies from 8.793 to 8.869A, as a result of the entry into the crystal structure of small amounts of water, depending on the pressures and temperatures applied.

Introduction

The natural fluorine end member of fluoborite was found first by Scacchi (1881) in the deeply metamorphosed ejecta of the "Tufo Campano"[1] between Sarno and Nocera Inferiore (Salerno, Italy). This mineral was first classified by Zambonini (1919) as an oxyfluoride of calcium and magnesium and was named nocerite. Bauer and Bermann (1929) suggested that it could be the fluorine end member of the isomorphic series of fluoborite. Brisi and Eitel (1957), by a comparative X-ray powder pattern examination of nocerite and of the synthetically prepared $Mg_3(BO_3)_2 \cdot 3MgF_2$, confirmed that nocerite is a member of the isomorphic series of fluoborite, $Mg_3(OH,F)_3(BO_3)$. Flamini (1966) showed that calcium, found in the chemical analyses of nocerite, belongs to impurities of fluorite closely associated with the mineral.

A review of the data found in the literature (Brisi and Eitel, 1957) showed a significant difference between the temperature used for the synthesis at atmospheric pressure of $Mg_3(BO_3)_2 \cdot 3MgF_2$ and that necessary for the formation of nocerite. It was therefore deemed appropriate to determine, by synthesis experiments, the extent to which certain factors, such as pressure and the presence of water, affect the temperature of formation of this mineral.

Materials and methods

For the synthesis of the fluorine end member of fluoborite, we used a mixture of magnesium ortho-borate and magnesium fluoride, $Mg_3(BO_3)_2 + 3MgF_2$. Magnesium orthoborate was previously synthesized by heating to 900°C for 48 hours a mixture of magnesium and boric oxides in the ratio of 3:1. The fluoborite synthesis experiments were performed at temperatures of 300, 400, 500, 600, 700, and 750°C and at pressures of 1, 250, 500, 1000, and 1500 atm. Temperatures were continously monitored by means of a chromel–alumel thermocouple. The duration of the experiments was six days. The experiments were performed both in anhydrous conditions and in the presence of water, sealing the mixtures into welded capsules (Ag: 70 percent, Pd: 30 percent). For the synthesis at atmospheric pressure an electric oven was used.

Results

Optimal conditions for the synthesis at atmospheric pressure were found to be a temperature of 750°C and a three-day duration of the experiment. At lower temperatures the reaction proceeded imperceptibly, while at higher temperatures fluoborite decomposed, as was shown by TG and XRD analyses (Fig. 1).

When the material was heated to more than 750°C, a progressive weight loss occurred and MgO and $Mg_2B_2O_5$ formed together with fluoborite. Applying pressure, it was found possible to obtain fluoborite also at temperatures considerably lower than 750°C. Indeed, under 250 atm pressure, fluoborite was formed, both in the absence and in the presence of water, at a temperature as low as 400°C. Fluoborite was obtained also at 300°C under pressures from 250 to 1500 atm, but only from mixtures reacted in the

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[1] The "Tufo Campano" is a pyroclastic formation related to the Phlaegraen Quaternary volcanic activity.
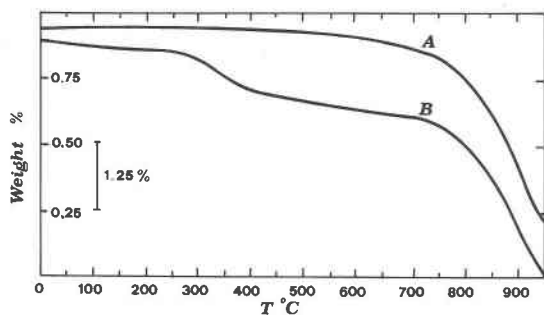
Fig. 1. TG curves of fluoborite (A) synthesized in anhydrous conditions, and of fluoborite (B) synthesized in presence of water at 1500 atm and 400°C.
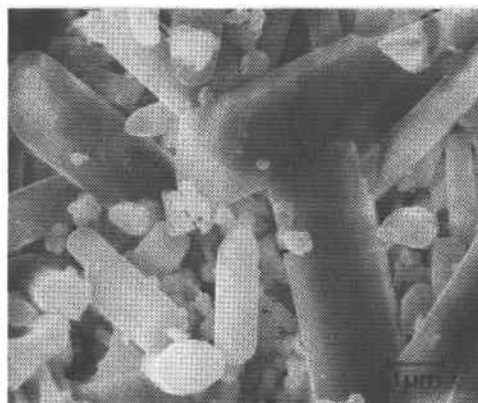

Fig. 2. SEM micrograph of fluoborite crystals, synthesized in anhydrous conditions at 1500 atm and 400°C.

absence of water. In the presence of water the mixtures virtually did not react.

XRD performed on the fluoborites obtained under the different experimental conditions showed that those formed in the presence of water exhibited variations in the a parameter of the unit cell. Table 1 illustrates the variations of a as a function of the pressure and temperature conditions under which the syntheses were performed in the presence of water. By mass-spectrometric and thermogravimetric analyses it was found that the expansion of the crystal lattice was due to water emitted when the material was heated to about 350°C at one atmosphere. The maximum amount of H_2O contained in the mineral prepared at 400°C and 1500 atm was found to be about 0.6 percent. After heating, the fluoborites showed the same lattice constants as those prepared in the absence of water.

SEM observations show that synthetic fluoborite occurs as elongated prismatic crystals, about 7 × 3 μm, similar to natural ones (Fig. 2).

Discussion

The results obtained in fluoborite synthesis experiments show that pressure, even if moderate, will sig-

nificantly decrease the temperatures required for the formation of this mineral. This explains why dry atmospheric-pressure syntheses of the fluorine end member of fluoborite require a temperature as high as 750°C while nocerite, the mineral whose composition is closest to this phase, can form at lower temperatures. The nocerite formation temperatures, deduced from the various paragenetic associations and from the different degrees of metamorphism undergone by the limestone blocks enclosed in the "Tufo Campano" may be estimated to be less than 500°C. Indeed, nocerite is abundant not only in these blocks of tuff, where the limestone fraction has almost completely disappeared, but also in blocks where heat caused only a partial recrystallization.

Note further that the crystal lattice of fluoborite synthesized in the presence of water shows a variation of the a parameter of the unit cell related to the pressures and temperatures applied for the synthesis. Because tubes along the c axis were found in the structure of fluoborite (Dal Negro and Tadini, 1974; Takeuchi, 1950) a "cavity-searching" was performed using a computer program written by Basso and Della Giusta (1977) and employing the crystallographic data for nocerite presented by Dal Negro and Tadini (1974).

A three-dimensional map of the minimum distances between each point of the unit cell and the nearest atom was drawn. It clearly shows that around the c axis is an almost cylindrical cavity with a diameter varying from 4.6 to 5.0A. Each point of the c axis is therefore distant not less than 2.3A and not more than 2.5A from the nearest atom, which is always a fluorine.

From Table 1 it appears that the increase in the a parameter of the unit cell, due to the entry of water, is

Table 1. Variations of the a parameter for the fluorine end member of the fluoborite series, synthesized in the presence of water

T°C	a (A)			
	P atm			
	250	500	1000	1500
400	8.823	8.839	8.854	8.869
500	8.816	8.823	8.831	8.831
600	8.808	8.808	8.823	8.823
700	8.793	8.793	8.808	8.808

made easier by increase in pressure, while it is hindered by increase in temperature. This parameter varies, in the fluoborite isomorphic series, also as a function of the content of $Mg_3(BO_3)_2 \cdot 3Mg(OH)_2$.

It could therefore be assumed that a reaction of the type $H_2O + F^- = HF + OH^-$ had occurred, and this would favor the formation of members with a variable content of $Mg_3(BO_3)_2 \cdot 3Mg(OH)_2$. It is believed that this reaction did not occur, however, because the replacement of OH^- with F^- is so small that variations of the a parameter should be much smaller than those observed (Flamini, 1966). Moreover, when this substance is heated to 350°C, together with the loss of water, a partial decomposition of the compound should occur, as when fluorine is lost at about 700°C. XRD analyses of the heated substance, however, did not show any sign of decomposition, so the interpretation of the phenomenon, by means of the entry of water in the tubes of the fluoborite structure, appears to be valid.

Thus, when the chemical composition of the mineral is to be correlated with the variation in the a parameter, it is essential to know whether interstitial water is present in the structure. The determination of the amount of water also makes it possible to estimate more accurately the genetic conditions of fluoborite.

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