

## HYDROTHERMAL-METASOMATIC BARITE FORMATION IN CARBONATE ROCKS (experimental models)

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The largest commercial barite concentrations occur in hydrothermal-metasomatic deposits confined to sedimentary rocks (first of all, carbonate rocks). The ore is formed chiefly at the expense of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  supplied to the metasomatic zones by strongly mineralised fluids. Barite is deposited when these fluids react with the carbonate rock horizons favourable for the ore accumulation at temperatures within the 100-300°C range.

The purpose of our experiments was to model formation of barite (Bar) and accompanying minerals - fluorite (Flu) and quartz (Q), and to find out the most favourable conditions for the formation of different types of barite ore. The experiments involved fluids of different compositions and pH factors and were conducted at temperatures from 150 to 350°C.

At the first steps of the experiments, we mostly made use of mixtures of  $\text{Na}_2\text{SO}_4$  and  $\text{BaCl}_2$  solutions with concentrations close to those of barite-forming fluids. At 250°C, we obtained a metasomatic column with two zones, a barite zone and a transient one (fig. 1).

The former consisted of barite with some quartz which content reached its maximum at the zone boundary. In the transient zone, barite filled the intergranular spaces and voids in calcite (Calc). Interaction of Ba- and  $\text{SO}_4$ -bearing acid chloride solutions with limestones produced barite mineralisation at  $t=150-300^\circ\text{C}$ ; at higher temperatures, no barite was observed (fig. 2). The interaction of carbonate rocks with neutral barium-bearing solutions ( $\text{H}_2\text{O}$ ) did not produce barite, the transformation being expressed in the washout of Si and Fe and a weak calcite recrystallisation (fig. 2).

In the barite-bearing zones, barite occurs in the impregnated form. At the front of metasomatism, the rocks are strongly corroded, calcite recrystallised. Four zones have been recognised within the metasomatic column: barite, barite-quartz with pyrite (Pyr), barite-quartz-calcite, and barite-quartz-calcite-pyrite. The major role in the formation of the metasomatic columns is played by opposed diffusion of barium, calcium, silicon, and iron. Barium is supplied by the fluid, and all other components are washed out from the carbonate. The ability of Ba and Si to migrate falls with rising temperature, while that of iron increases. The metasomatic columns become thinner with a rise in the temperature (1.8 times from 150 to 200°C).

The Flu-Bar association is formed when the carbonate rock comes into contact with moderately acid  $\text{Ba}^{2+}$ - and  $\text{SO}_4^{2-}$ -bearing fluoride solutions throughout the entire temperature range (150-350°C); this process is particularly active at temperatures below 200°C, while higher temperatures stimulate active fluorite formation.

The Flu-Bar-Q mineralisation is produced by the interaction of the carbonate with  $\text{Ba}^{2+}$ - and  $\text{SO}_4^{2-}$ -bearing silicon-fluoride fluids. The metasomatic columns are thin (0.25-0.50 mm), with one or two zones. In contrast to the experiments with purely fluoride solutions, a rise in the temperature brings about an increase in the Bar content in the metasomatic columns. Silicon, barium, and iron are supplied to the front of metasomatism at  $t=150-250^\circ\text{C}$ , giving rise to a peculiar zone of pre-ore alteration of the host rock, thickness of the zone falling with increasing temperature.

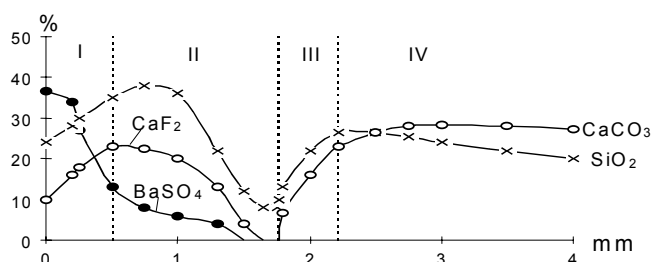


Fig. 1. Barite-fluorite-quartz metasomatic zoning in carbonate rocks. Zones: I - barite; II - barite-quartz- fluorite; III - quartz-calcite; IV - unaltered limestone

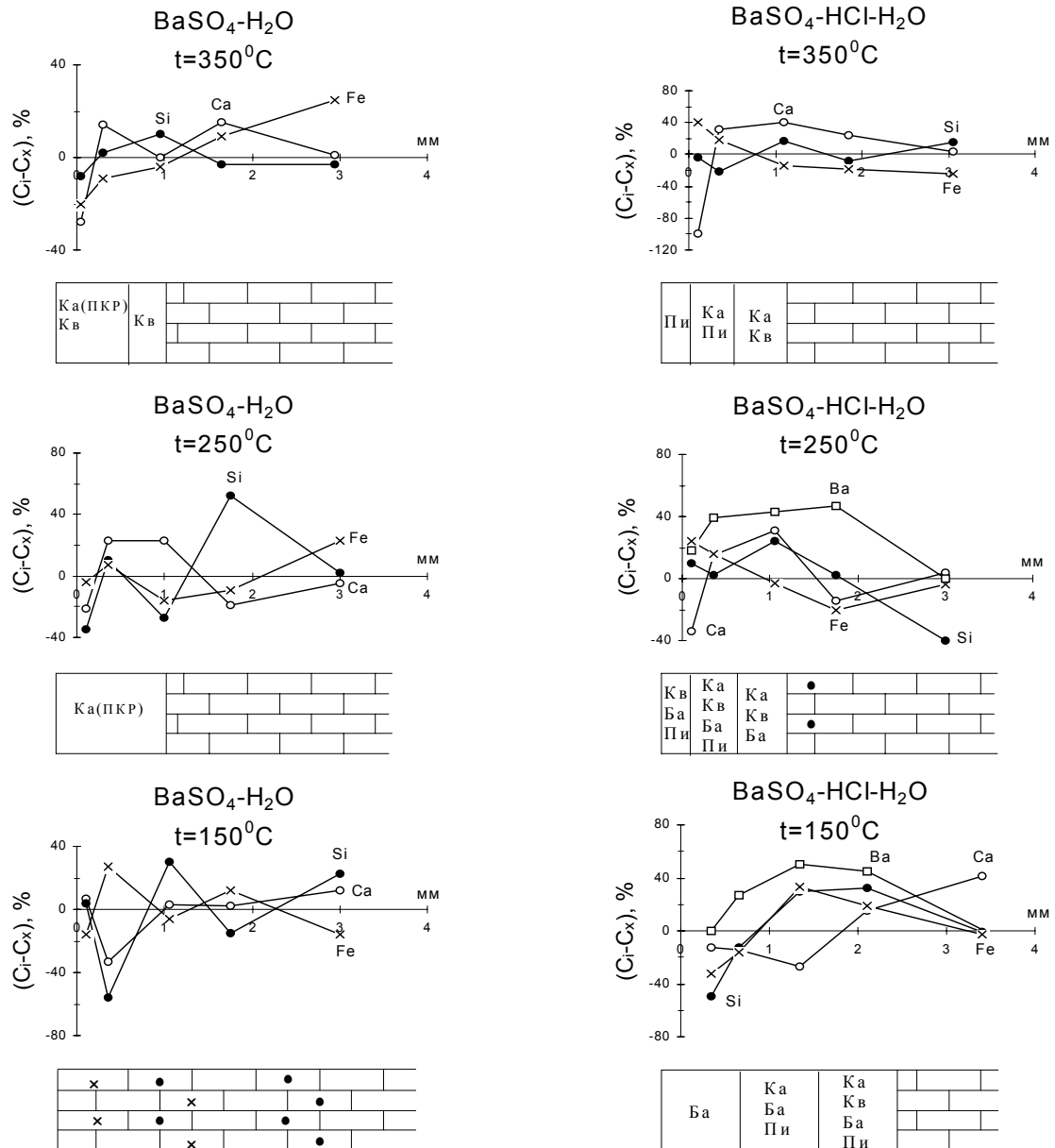


Fig. 2. Metasomatic alteration of limestones under the action of  $\text{Ba}^{2+}$ - and  $\text{SO}_4^{2-}$  bearing hydrothermal fluids