GEOLOGICAL SITUATION AND PROCESSING POSSIBILITIES OF THE RARE EARTH ORE OF DONG PAO/VIETNAM

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The mineral bastnaesite is an RE (Rare Earth) fluorite-carbonate. As a processing concentrate of 60-70 % RE-oxides it is used on a large scale for the production of RE-metals and their compounds. The world's largest deposit of bastnaesite is situated near Bayun Obo/China, on the northern edge of the Chinese Plateau.

On its southern edge, in the Lai Chau Province in the extreme north-east of Vietnam, there are various deposits of rare earth ores as well, although much smaller in extent and less well known. The deposits at Dong Pao are regarded as the most significant ones among them.

The surrounding mountain region is inhabited by national minorities. The infrastructure is little developed. The Vietnamese side is interested in developing the area on the basis of the existing raw materials. In the former Soviet Union and in China besides geological investigations, techniques concerning the processing of ore samples from the Dong Pao deposits had already been undertaken during the 1960s and 1970s; in the 1980s another stage of investigations began under the leadership of experts from the then German Democratic Republic (GDR), with its planned economy.

Processing of Dong Pao ores were carried out in the context of investigations, ranging from laboratory to the semi-technical scale. Decisive roles in these investigations fell to the Dresden Institute of Mineral Raw Materials (now the firm of Rohstoff Consulting Dresden GmbH), to the FIA Processing Research Institute at Freiberg, and to the then VEB Agrochemie Piesteritz (now the Piesteritz Nitrogen Works AG).

The aim of these studies was to develop a method of processing the RE that would be practicable under the conditions of the location, permitting production of a drilling-grade barytes.

Some observations on the geology of the deposit

The Dong Pao deposit is on the borderline between the Phangsipang anticlinal structure and the Da River. The boundary between these structures is tectonic in nature, and is evidently marked by a deep-seated system of disturbances.

The area of the deposits is characterized by the development of ferruginous carbonatic sediments, the immediate frame of the mineralization being almost exclusively formed on faunal avidence by the limestone from the Lower Muschelkalk (Middle Triassic) (T2a). Schist, shales and sandstones (T2b to T3) occur sporadically, and at times even contain smallish lenticular or wedge-shaped deposits of coal. As a result of folding during tectonic processes, the limestones have undergone considerable cracking, crushing, and metamorphosis into dolomite marble. The geological development of the area was decisively affected by the occurrence of paleogenic volcanism of the alkaline rock, which is found predominantly in conjunction with deep-seated fault disturbances.

The majority of the magmatites consist of syenite intrusions; however, they also occur in the form of effusive rocks, in which case they tend to appear as trachytes. Continuous transitional forms like syenite and trachyte porphyries are described as lying between the intrusive syenites and the effusive trachytes. A wide variety of dyke rock formations are classified as belonging to the same Pusan Cap complex; as schonkinites and vogesites their chemical composition also shows a marked resemblance to the alkaline rock magmatites described above.

The formation of numerous carbonatite passages with fluorite, barytes, and an RE-mineralization is to be seen as a spatially, and probably also a genetically, close relationship to syenites and trachytes. This conclusion is further supported by the impregnative formation of the latter minerals which one observed. The formation of zonally-constructed ore-bodies (RE-barytes, RE-barytes-fluorite, barytes) speaks for the view that ore formation is evidently the result of a multi-phase process. The ore bodies present a complicated structure. The morphology of their surface construction can be best likened to a stick-like, isometrically shaped ore body, although data on their extent in terms of depth are unfortunately not so far available. On the other hand, small ore bodies present a characteristic, passage-like form, and tend to sit on the two main fault-lines (NW 300 to 330°, or NE 10 to 30°.

Fig. 1 shows a schematic geological sketch of the central section of the Dong Pao deposit.

As a result of process of thorough weathering, a deep supergenic alteration of ore-bodies occurred and, as a matter of principle, affected all the ore

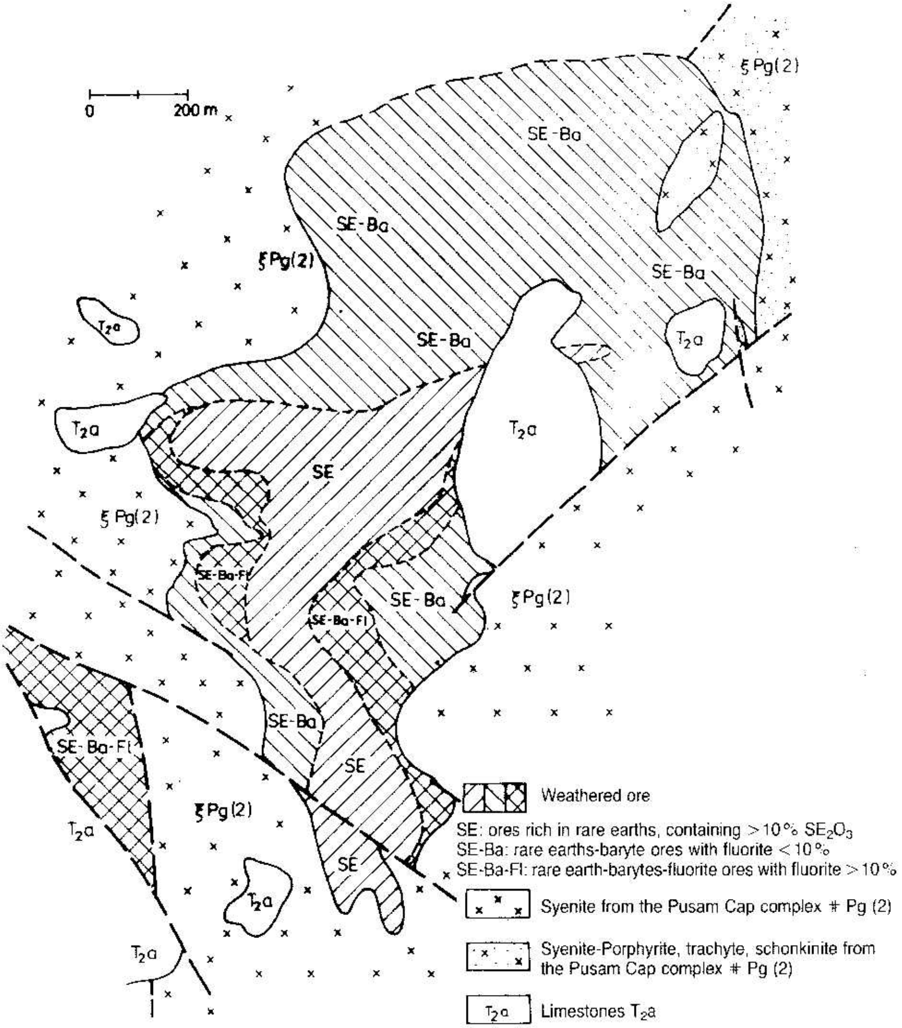

Fig. 1 – *Schematic map of the Dong Pao deposit. Explanation in the text.*

minerals, albeit in different ways. During weathering the extremely finely grained RE-minerals, which formed the matrix, proved to be the most unstable and were decisive for the altogether earthy appearance of the "weathered ore". Within the earthy weathered ore, which has frequently undergone a stocking-up in respect of the concentration of its RE content, major relics of plate-like barytes and isometric bodies of fluorite may be found. The degree of weathering tends to decrease continually with increasing depth. Within the context of

Table 1 – *Chemical composition of the Dong Pao crude ores as shown in the examples of mixed samples selected for processing experiments (in %)*

SE_2O_3	$BaSO_4$	CaF_2	SiO_2	$CaCO_3$	Fe_2O_3	MnO	SrO	Pb	Zn	Nb	U
14.6	51.6	10.3	8.4	2.9	2.2	1.3	0.46	0.42	0.11	0.03	0.03
8.9	43.4	29.3	4.1	0.8	1.8	2.6	0.65	0.36	0.05	0.03	0.03
8.0	39.5	30.2	8.5	2.5	2.4	n.b.	0.64	0.15	0.18	0.02	0.02

these investigations it was not possible to observe the transition to the merely slightly decomposed probable primary ore in more than 2 out of 13 prospecting shafts, which had been opened up to a maximum final depth of 30m. This solid ore consists of approximately the same mineralization (RE-barytes-fluorite), with a perceptible amount of calcite added to it.

Characterization of ores

The Dong Pao deposit contains ores of varying degrees of weathering, which have evolved from carbonatitic basic rock, and laid down in the surface region almost like strata. The chief mineraliferous rare earth is bastnaesite. Much less prevalent are other RE-fluorite carbonates. Cerianite, too, has been spotted. Associated minerals are above all baryte and fluorite. In addition, the ores contain among others quartz, oxidic Fe and Mn minerals, as well as a small amount of calcite. Findings of ores not decomposed by weathering remained few and far between; they did, however, contain considerable quantities of calcite. Table 1 shows the chemical composition of the weathered ores by way of selected mixed samples.

The main body of ore from the deposit under investigation contains 3 sorts of ore: they are characterized as follows:

Sorts of ore:	I[1]	II[2]	III[3]
SE_2O_3	13.9	5.0	5.8
Fluorite	22.8	6.1	29.9
Barytes	42.5	57.8	42.4
Proportion of ore reserves	39.5	31.8	28.7

[1] Substantial weathering, rich in bastnaesite.

[2] Weathered, less rich in bastnaesite, poor in fluorite.

[3] Weathered, poorer in bastnaesite, rich in fluorite.

Table 2 – *Structure of grain sizes, together with distribution of RE depending upon grain size, as demonstrated by a mixed sample of ore type I*

Grain size in mm	Distribution in % Mass	SE_2O_3	Barytes	Fluorite	Assay in % SE_2O_3	Barytes	Fluorite
< 0.015	16.8	43.9	7.5	4.1	35.7	22.3	3.9
0.015 – 0.032	7.4	8.0	7.3	5.1	14.7	48.8	11.2
0.032 – 0.063	5.7	5.4	5.3	4.3	12.5	48.6	12.7
0.063 – 0.1	9.1	9.7	10.2	7.3	13.9	58.3	13.4
0.1 – 0.315	11.1	10.9	11.4	10.9	12.9	53.4	16.5
0.315 – 0.5	6.5	6.0	6.5	8.4	12.1	51.7	21.6
0.5 – 1.0	12.2	7.7	12.2	17.4	8.3	51.9	23.9
1.0 – 2.0	12.4	4.8	14.8	18.0	5.1	62.0	24.4
> 2.0	18.8	3.6	24.8	24.5	2.6	68.1	21.8
	100.0	100.0	100.0	100.0	13.1	51.9	16.8

The reserves of ore hitherto explored amount to 1.1 million tonnes. In this ore type I contains almost 2/3 of the rare earths of the parts of the deposit hitherto explored.

In the course of the laboratory tests it was established that two genetically conditioned qualities of the ores in particular are of crucial significance for solving the problem of processing. One of them is the process of heavy weathering, which causes a high proportion of mud, together with a marked dependency of the distribution of valuable material upon the grain size, and the other the compounding of bastnaesite and other RE-fluorite carbonates with fluorite. These minerals resemble one another greatly in respect of flotation properties, a fact that serves to complicate their separation in processing techniques. Based on the example of ores from Bayun Obo/China a number of publications on this problem have appeared in recent years.

As already mentioned above, the distribution of valuable material characteristic for the weathered ores of the deposit results in an addition of bastnaesite in the finest materials (Table 2). Some sections of the deposits near the surface were found to contain RE oxides in excess of 40% (more than 54 % bastnaesite!).

Processing of ores

The grain size-dependent distribution of valuable materials, as well as their "association" with fluorite, have hitherto prevented processing into marketable bastnaesite concentrates with about 60% RE oxides under economically justifiable recovery.

First attempts at processing by grading with hydro cyclones, however, have already succeeded in separating up to 50% of the RE in the ore slurry. Simultaneous metallurgical experiments with separated ore slurries yielded evidence that, under certain conditions and thanks to their specific qualities in processing, primary slurries with more than 25% RE oxides can be used to advantage for the extraction of the rare earths.

On the basis of proven possibilities of exploitation of the ore slurries, the following processing technique for the ore of type I has been developed and tested on a technical pilot scale.

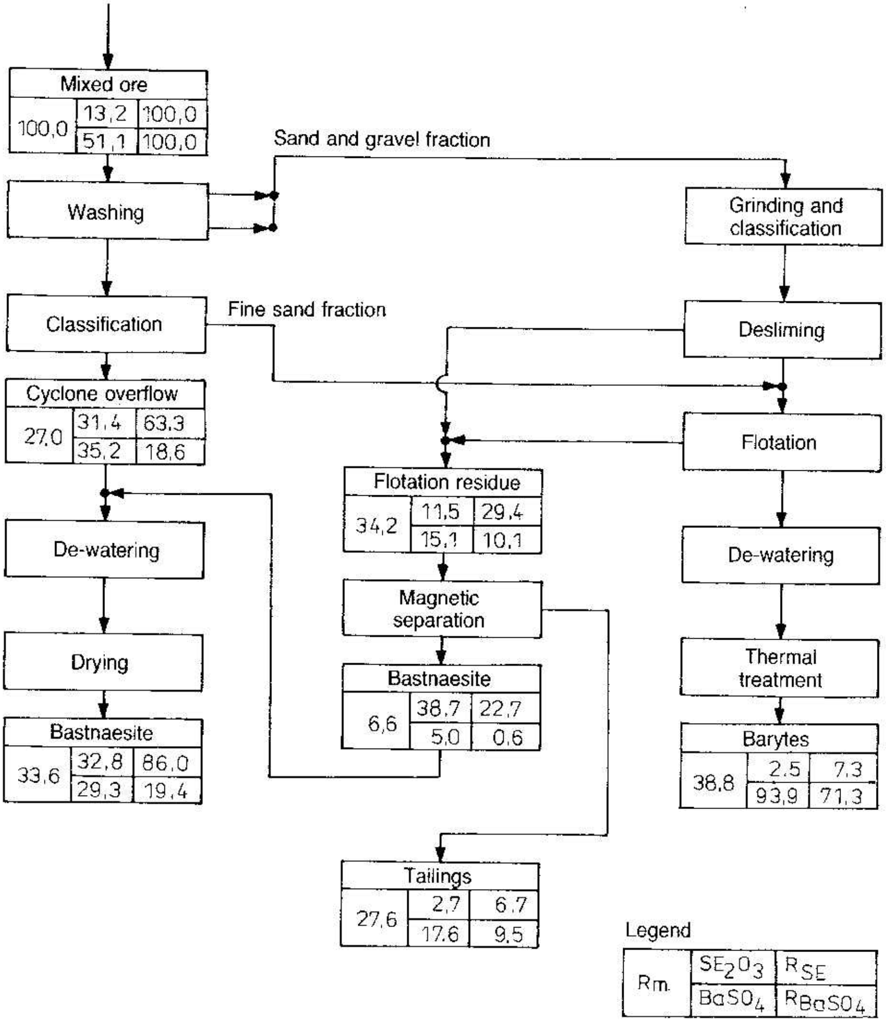

Fig. 2 – *Simplified process scheme for processing Dong Pao Rare Earth ores. Commentary in text.*

The parameters in the process scheme shown in Fig. 2 are based on results achieved with the ore samples available, and within the limits of the semi-technical experiments. These ore samples represent above all type I ore from the deposit.

Washing and classifying

According to technology, the run-of-mine ore is drawn from the crude ore bin to a vibrating wet screen of 40 mm sieve aperture. Having left the screen, the coarse oversize material undergoes a hand-picking process. The undersize mixed with the picking concentrate is led to a washing drum to liberate the bastnaesite. Thereby certain values of residence time and pulp density have to be maintained. Concluding from the pilot scale tests, a residence time of 40 minutes and a pulp density of 1550 g/cm^3 are favourable values.

After leaving the washing stage, the material is screened at 2.5 mm cut-size by means of a rotary screen. The fraction below 2.5 mm is delivered to a classifying circuit consisting of an upstream classifier and a spiral classifier. Via a surge bin, the overflow of the upstream classifier flows subsequently to a hydrocyclone arrangement. Simultaneously, the classifier underflow flows to the spiral classifier, separating the remaining fines as a scavenging stage. As additional rinsing-water, the spiral classifier overflow is circulated to the rotating screen.

Aiming at maximum recovery of the fine fractions in the hydrocyclone stage mentioned, the hydrocyclones are connected in a special manner as to be seen in Figure 3.

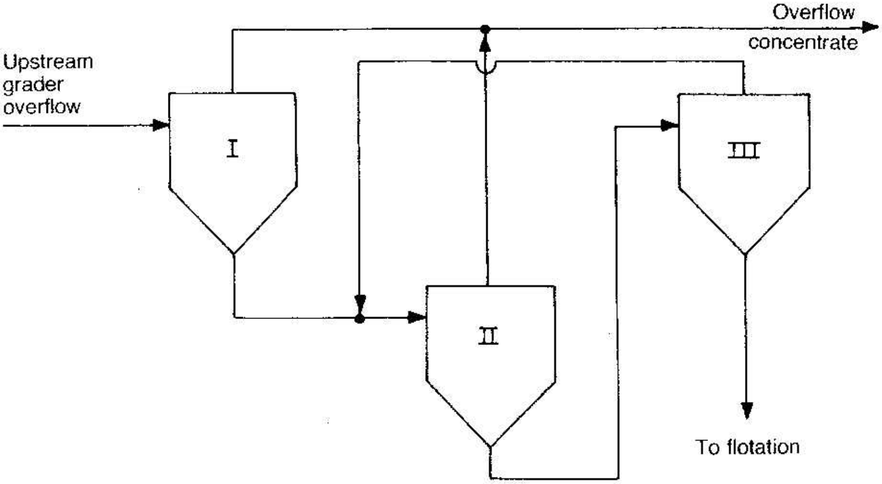

Fig. 3 – *Flow chart of the hydro-cyclone stage of the purification. Commentary in the text.*

Table 3 – *Composition of the mixed bastnaesite concentrate (in %)*

SE_2O_3	$BaSO_4$	CaF_2	SiO_2	Fe_2O_3	MnO	U	Th	Cu	Pb	Zn	Nb
32.8	29.3	7.5	4.6	6.0	3.3	0.04	0.04	0.02	0.33	0.27	0.07

At a cut size of 0.015 mm, the overflow of the first two hydrocyclone stages yields the valuable product.

Adding a flocculant to the overflow product prior to being pumped to the thickener has proved beneficial. The thickener slurry is dewatered subsequently by filter presses down to about 25% residual moisture. The thickener overflow water and the water from the filter presses can be used as recycling water.

The specific water consumption of the total washing stage without any recycling of water is designed to be about $19 m^3/t$.

For the drying of the filter cake, a rotary dryer can be used. The filter cake has proved to show favourable drying properties. While passing through the rotary dryer, the cake pieces are formed to ball-shaped agglomerates with only 5% fines below 0.04 mm grain size.

The dried product contains about 31% RE-oxides. The RE-recovery attains 63%.

In addition to bastnaesite (42%), the first bastnaesite concentrate contains above all baryte (about 35%) and fluorite (about 8%). Furthermore, there are concentrated the Mn- and Fe-oxides of the ore, causing a brown colour. The composition of the first bastnaesite concentrate is shown in more detail in Table 3.

$BaSO_4$ flotation and magnetic separation of bastnaesite

The washing stage residue consisting of the screen oversize > 2.5 mm (gravel fraction), the spiral classifier coarse fraction 0.1-2.5 mm (sand fraction) and the underflow of the third hydrocyclone stage 0.015-0.1 mm (fine sand fraction) can be used to produce drilling grade baryte.

Thereby, prior to flotation, the gravel and the sand fractions are mixed and fed to a grinding circuit consisting of a spiral classifier and a ball mill, grinding the feed material down to below 0.16 mm. Subsequently the overflow of the spiral classifier is deslimed and added to the fine sand fraction of the third hydrocyclone stage. Prior to being fed to the rougher flotation, the material is pumped to a surge tank and adjusted to a pulp density of 1.42 g/l. The residue of the rougher flotation stage flows to the scavenger flotation. The froth product of the rougher flotation is re-cleaned twice. Being very stable, the froth product of the second cleaning stage is directly delivered to the dewatering by filtration.

The flotation agents to be used are the following ones:

– FAS-paste	500 g/t
– sodium silicate	750 g/t
– lignin sulfonate	100 g/t
– petroleum	1,000 g/t

Sodium silicate and ligninsulfonate are used as depressants for fluorite, bastnaesite, quartz and oxides. FAS-paste is a technical product of the Fettchemie chemical works at Chemnitz, consisting of a mixing of C10 up to C20 sodium alkyl sulphates. Emulsified with petroleum it is applied for collecting baryte. Thereby it has proved beneficial to adjust the pH-value to about 9-9.5. At lower pH values fluorite and bastnaesite tend to float along with the baryte.

The flotation process described yields a concentrate of about 94% baryte and bastnaesite and fluorite 3% each. Having undergone a heat treatment to decompose the adhering flotation agents the baryte concentrate can be used to produce baryte for drilling mud. The flotation recovery of baryte achieves 87%. Losses of baryte of 11% are caused above all by the necessary desliming process prior to flotation.

The mixture of flotation tailings and grinding slimes still contains about 15% bastnaesite. It has proved useful to treat it by high intensity magnetic separation. By a single wet magnetic separation process on a magnetic testing installation with steel ball matrix, a concentrate with 38.7% RE-oxides could be obtained. This product can be mixed with the first bastnaesite concentrate. Due to the additional magnetic separation stage, the total RE-recovery can be increased to 86%.

This process of preparation does, of course, allow for the omission of the barytes flotation and the direct feeding of the residues from washing to magnetic separation. It would be possible to use only the fine sand product, as it contains c. 75% of the RE-content of the washing residue and shows a favourable feed grain size for magnetic separation.

It is worth mentioning that the fluorspar contained in the ore, which occurs in a greatly enriched state in the processing residue, can be extracted from it by flotation. Developed at the scale of the laboratory, a reagent system with a collector on the basis of unsaturated C16 - C18 fatty acids was set up, which permits direct flotation of fluorite even at higher bastnaesite contents. In the process waterglass, lignin sulphates and sodium silico-fluoride were used as depressants for bastnaesite and gangue minerals. The flotation process depends greatly on pH. An acceptable separation efficiency was obtained only in a narrow pH range between approximately pH8 and 8.5.

Table 4 – *Composition of the RE-oxides of the bastnaesite concentrate (in %)*

Y_2O_3	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
0.5	37.2	47.1	3.7	9.7	0.8	0.2	0.4

Fluorite concentrates of more than 90% CaF2 could be floated out of baryte flotation residues of about 35% fluorspar content by laboratory cycle tests with three cleaner stages.

Metallurgical processing of bastnaesite concentrates

The mixed bastnaesite concentrate shows the parameters listed in Table 3.

The distribution of the RE-elements in the RE-oxides is presented in Table 4.

A high proportion of waste rock is not favourable to metallurgical processing by traditional processes, which include the acidic leaching of the concentrate as a first stage.

When treating the purification concentrate with sulphuric acid it was noted that under certain conditions the process of leaching decomposition runs in a practically solid phase. This phenomenon is attributed to the specific structure and composition of the concentrates, which cause – amongst others – a certain ability to soak up sulphuric acid. The dry process of decomposition can be carried out at comparatively low temperatures of only 200-300°C.

Based on the results of this investigation, an unconventional metallurgical process for the decomposition of bastnaesite concentrates was developed. According to this process of decomposition, the dried bastnaesite concentrate is comminuted and processed by a combination of the following steps in the process:

- mixing with a certain quantity of concentrated sulphuric acid to a practically dry granulate, as a result of exothermal reaction.
- heating of the granulate to a temperature of 200-300°C in order to expel the fluorine (this stage of the process benefits from being carried out in rotating drums).
- dissolving of the RE sulphates and of the Fe sulphate by means of cold water.
- separation of the undissolved constituent parts of $BaSO_4$, $CaSO_4$, SiO_2, MnO_2 by filtration.
- precipitation of the Rare Earths as Na RE-bisulphate, and separation by filtration.

- chemical change of the Na RE-sulphates to rare earth hydroxides with the help of caustic soda, and separation from the sodium sulphate solution by filtration.
- treatment of the accumulating filtrates with NaOH and means of oxidation and soda ash for removing the proportions of Fe^3+, Mn^2+, Zn^2+, Ca^2+ and other bi-valent metals by precipitation with NaOH and filtration.
- regaining the sodium sulphate from the filtrates by cooling, crystallization, filtration or centrifuging.

The studies were broken off in 1990, as there was no longer any demand for Vietnamese bastnaesite in the economy of the former GDR after German reunification.

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