Carbonate metasomatism of oceanic lithosphere and carbonate-silicate-sulphide liquid immiscibility

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Mantle metasomatism is a very powerful process of global differentiation. The large-scale transportation of material in the upper mantle is closely connected with the origin of alkaline magmatism. For instance we investigated the isotopic signature of Kola Peninsula alkaline rocks (Kogarko *et al* 1986) and related gigantic rare metal deposits. These data demonstrated that they originated from a quite depleted mantle source. So there is a paradox: on the one hand these rocks are extremely enriched in rare elements, on the other, they have a depleted mantle signature. The enormous concentration of rare elements in alkaline rocks of this region is mostly related to large-scale processes of mantle metasomatism and is confined to a very narrow time span (371–361 Ma) so the primary signature stayed unchanged. There are many chemical types of mantle metasomatism. During many years we carried out the investigations of metasomatised mantle material from different regions of the globe. The petrologic and geochemical study of lherzolitic and harzburgitic xenoliths from melilitites of Montana Clara island (Canary archipelago) and basanites of Fernando de Noronha island revealed that oceanic mantle of these regions has been affected by very strong carbonate metasomatism. Partial melting of carbonated metasomatized mantle results in carbonate-silicate-sulphide liquid immiscibility, which has been confirmed by our experiments.

Metasomatized mantle material from Montana Clara Island

During the investigation of harzburgite nodules from the Montana Clara volcano (Canary archipelago), evidence of primary carbonate melt was found. This carbonate is enriched in calcium and it occurs together with glass containing sulphide globules. In addition to primary olivine and orthopyroxene, there are pockets of fine-grained minerals belonging to the metasomatic second generation (more magnesian olivine, sodium-bearing clinopyroxene, less aluminous spinels). The metasomatic assemblage was formed by reaction of sodium-bearing dolomitic

TABLE. 1. Composition of melt inclusions in Ol from mantle nodule (Fernando de Naronha)

Sample	SiO_2	TiO_2	Al_2O_3	FeO	MnO	Cr_2O_3	NiO	MgO	CaO	Na_2O	K_2O	SO_2	Total
Carb. inc.	0.32	0.01	0.01	0.31	0.03	–	0.03	1.00	52.43	0.11	–	–	54.25
Sulph. incl.	0.32	0.01	0.01	32.65	0.03	–	32.50	–	–	0.11	–	33.97	99.60
Glass. incl.	57.47	1.02	25.42	1.56	–	–	–	–	0.97	9.04	3.87	–	99.35

melt with harzburgite according to the reactions:

$$4MgSiO_3 + CaMg(CO_3)_2 = 2Mg_2SiO_4 + CaMgSi_2O_6 + 2CO_2 \quad (1)$$

$$3CaMg(CO_3)_2 + CaMgSi_2O_6 = 4CaCO_3 + 2Mg_2SiO_4 + CO_2 \quad (2)$$

The calciocarbonatite and sulphide phase almost invariably form globules in the silicate glass indicating the existence of three immiscible liquids under upper mantle conditions, resulting from melting of the metasomatised mantle material during uprising and adiabatic decompression. Therefore the investigated mineral assemblage, including carbonate and glass, can be considered as a micro model for the generation of Ca-rich carbonatitic magmas during the processes of the partial melting of carbonatized oceanic mantle.

Intense carbonate metasomatism of the oceanic mantle beneath Fernando de Noronha island

Petrologic and geochemical study of lherzolitic and harzburgitic xenoliths from basanites of Fernando de Noronha island revealed that oceanic mantle of this region has been affected by very intense carbonate metasomatism. The metasomatism led to a wehrlitization according to reaction (1) of the primary harzburgitic minerals assemblage (Ol, OPx, Sp) and to an increase of the Mg/Fe ratios of the minerals. The wehrlitization was the result of interaction between an ephemeral sodic dolomitic melt or fluid with the harzburgitic rock according to the reactions(1) and (2). This model is in agreement with the experimental results of Dalton and Wood (1994). Olivines have abundant polyphase, glass-rich inclusions, consisting of phonolitic glass, monosulphide of Fe, Ni, and Cu, Ca-rich carbonate (Table 1) and dense CO_2. All major silicate phases of the rocks are rich in CO_2 inclusions. The interrelationships between glass, sulphide and carbonate inclusions permit speculation, that silicate, sulphide and Ca-rich carbonatite melts were in equilibrium with each other and originated from partial melting of metasomatized and wehrlitized mantle of Fernando de Noronha island. We have experimentally investigated, with a piston-cylinder apparatus, the immiscibility relationships in the system Ca-rich carbonate – Fe, Ni sulphide – silicate melt of phonolitic composition, containing F. Experiments were made at 1250° C and 4–15 kbar. The double-Pt-capsule method has been employed in order to control the oxygen fugacity. Immiscibility has been observed in the investigated system as a complete separation of the carbonate and silicate liquids, with sulphide melt present in the form of small globules in both liquids. The sulphur solubility in the silicate melt varies from 0.15 to 0.35% and in carbonate liquid from 0.02 to 3.7% depending on the alkali content.

Conclusion

The results obtained allow the development of a two stage model of Ca-rich carbonatite formation: 1st stage - metasomatic wehrlitization and carbonatisation of mantle rocks; 2nd stage - partial melting of the wehrlitic substrate containing carbonates, resulting in two liquids and the generation of calciocarbonatites. If the sulphur concentration was high in metasomatized mantle material three immiscible liquids could be produced. The development of carbonatite magmatism on Canary Islands, Cape Verde Islands is likely to be related to the partial melting of carbonatized mantle in the South Atlantic, which took place over an extensive area.

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