Preliminary data on the stability of fillowite-type phosphates: an experimental investigation of the $Na[Mn,Fe(II)]_4(PO_4)_3$ system

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Fillowite and johnsomervilleite are Na-, Mn- and Fe-bearing phosphate minerals, with simplified chemical compositions $Na_2CaMn_7(PO_4)_6$ and $Na_2CaFe^{2+}{}_7(PO_4)_6$, respectively. They occur as primary phases in granitic pegmatites, in meteorites and in metamorphic rocks. The fillowite-type structure is trigonal, space group R-3, with a = 15.28 Å, c = 43.51 Å, and Z = 18 [1].

In order to understand the stability of fillowite-type phosphates, the $Na(Mn_{1-x}Fe^{2+}{}_x)_4(PO_4)_3$ system (x = 0, 0.25, 0.5, 0.75, 1.0) was synthesized under hydrothermal conditions, between 400 and 700°C, at 1 kbar. For x = 0.0, single-phase fillowite is obtained between 400 and 700°C, whereas the incorporation of iron provokes the crystallization of alluaudite $[Na_2(Mn,Fe^{2+})_2Fe^{3+}(PO_4)_3]$ and sarcopside $[(Fe^{2+},Mn)_3(PO_4)_2]$, associated with fillowite (400–600°C, x = 0.25, 0.5, 0.75). For x = 1.0, an assemblage alluaudite + maricite $[Na(Fe^{2+},Mn)(PO_4)]$ + sarcopside occurs at all temperatures. At 700°C, the proportions of alluaudite-type phosphates significantly increase, compared to the experiments at lower temperatures. This feature probably results in an oxidation of iron, favoured by the increase of hydrogen diffusion through the gold capsule at high temperatures.

The electron-microprobe analyses show an increase of the $Fe_{tot.}/(Fe_{tot.}+Mn)$ ratio with temperature, from $Fe_{tot.}/(Fe_{tot.}+Mn)$ = 0.337 (400°C), to $Fe_{tot.}/(Fe_{tot.}+Mn)$ = 0.514 (700°C). At 600°C, the iron-richest fillowite-type phosphate has been observed, with a composition $Na_{2.24}Fe^{2+}{}_{3.79}Fe^{3+}{}_{0.61}Mn_{3.17}(PO_4)_6$, and a $Fe_{tot.}/(Fe_{tot.}+Mn)$ ratio = 0.581.

Correlations between the Fe contents and the unit-cell parameters have also been established. The unit-cell parameters decrease when $Fe_{tot.}/Fe_{tot.}+Mn$ increases, and the decrease of the c parameter is more pronounced than the decrease of a. This behaviour is related to the topology of the fillowite structure, in which the M sites are aligned along the c axis.

[1] Araki, T. & Moore, P.B. (1981). Am. Mineral. 66, 827–842.

The Kusa gabbro massif (the Southern Urals): Sm-Nd isotope and geochemical constraints

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The Kusa gabbro massif forms a part of the Middle-Riphean Kusa-Kopan gabbro intrusion (the Southern Urals), locating in its north-eastern ending. Geology and petrology data on the Kopan, Matkal, Medvedev, Kusa massifs composing the intrusion and associated with them ilmenite-titano-magnetite deposits were repeatedly adduced in literature, however, Sm-Nd isotope age data up to now were absent. A result of our researches is an attempt to meet this lack. Summarizing the obtained Sm-Nd data it is necessary to note that the most representative one for the gabbro-norites of the north-western block is a data sampling with "probability fit" 0.22, containing figurative points of plagioclase, apatite, gabbro-norites, which determines Sm-Nd age of gabbro-norites as 1388±63 Ma. Addition of data belonging to grass contents of the south-eastern block gabbro-norites transfers an isochronal dependence (I model of York) into a category of errochrons one and leads to a corresponding decrease of "probability fit" that, possibly, is connected with heterogeneity of an initial Nd isotope ratio ($\pm 2\sigma$ initial $^{143}Nd/^{144}Nd$ variation=0.000023). The last one is indirectly confirmed by a number of petrographical and geochemical features of gabbro-norites of the north-western and south-eastern blocks. The north-western block gabbro-norites have high contents of Ni, Cr, Cu and U, they are also distinguished by higher ratios of Ni/Co (1.9–3 against 0.24), Cu/Co (3–5 against 0.7–0.8), Cu/Zn (1.6–2.2 against 0.09). For these gabbro-norites are also typical high contents of chlorine in apatites. The south-eastern block gabbro-norites differ by heightened contents of Fe, higher Ti/Fe ratios (0.34 against 0.16–0.19) in the background of close Fe contents, the lower degree of Fe oxidation, higher REE contents with a clear positive Eu anomaly, higher contents of K, Ca, P, Zr, Hf, Nb, Ta, Mn, Sr, Th, Zn and Pb, higher ratios of Th/U (6,7 against 1.8–3.8), Zr/Hf (30 against 15–20), La/Y (6 against 4–5). Higher Zn quantities in gabbro-norites of this group are determined possibly by their geochemical affinity with bivalent Fe, quantity of which is more here.