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Interaction between amphibolite and NaCl solution at 800-900°C and 5–7 kbar: experimental study

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Infiltration gain of alkalies, silica and subtraction of bases in granitization processes result in successive transformations of enclosed rocks. Andesine, oligoclase, potassium feldspar, and quartz substitute magmatic plagioclases (labradorites and bytownites) in magmatic metabasites. As the granitization extent increases, dark-colored minerals, clino- and orthopyroxenes, disappear completely being substituted by hornblende and biotite. Amphibole is a single mineral that is observed throughout the profile, from unaltered rocks up to shadow skialites of amphibolites in grantoids. This is due to iso- and heterovalent isomorphism in amphibole providing its stability at revolutions of fluid regimes and T-P conditions. Field studies show, that the total concentration of alkalies, K/Na ratio and the $X_{Fe} = Fe^{2+}/(Fe^{2+} + MgO)$ in minerals increases with increase of the extent of granitization. The highest X_{Fe} in amphiboles is observed in back zones of granitization columns. These zones represent the most altered enclosed rocks (debasificated and contained high potassium field). The highest molar concentration of chlorides (up to $X_{NaCl} = 0.3$ [*Khodorevskaya,* 2005]; $X_{NaCl} = 0.30$-0.35, $X_{KCl} = 0.20$-0.15 [*Korikovsky and Aranovich*, 2010] is also observed in these zones. The high iron content in minerals can not be due to high P-T conditions affected rocks. Experimental studies [*Helz,* 1973; *Wolf and Wyllie*, 1994; et al.] showed that the partial melting of metabasites at temperatures ranging from 750 to 900°C and pressures from 5 to 10 kbar results in the non-high $X_{Fe} \approx 0.2 - 0.5$. For this reason, high-ferruginous minerals are most likely formed as of consequence of their interactions with high-concentrated fluids. To verify this hypothesis, we conducted experiments on interactions of amphibolites with a fluid phase, representing a NaCl water solution at X_{NaCl} ranging from 0 to 0.5. Results of our studies are reported in this paper.

Materials and experimental techniques

We conducted experimental runs at temperatures from 800 to 900°C and pressure of 5 kbar using the high gas pressure arrangement with internal heating following to the quenching technique. A finely ground amphibolite (Amph) from the mafic dike of the Early-Proterozoic complex of early Pre-Cambrian field "Stanovaya" is used as a staring material. Major components of the amphibolite are plagioclase, An_{46} (from 25 to 30 mass %), and amphibole (≈ 70 mass %). The plagioclase composition is following: SiO_2 - 56.61, TiO_2 - 0.04, Al_2O_3 - 26.51, CaO - 9.46, Na_2O - 6.40, K_2O - 0.08; total: 99.10 mass %. The amphibole composition is: SiO_2 - 40.80, TiO_2 - 2.17, Al_2O_3 -11.47, FeO -17.22, MnO - 0.19, MgO - 9.57, CaO - 11.25, Na_2O - 2.62, K_2O - 1.46, Cl - 0.80, H_2O (loss on ignition) - 1.8; total: 99.35 mass %.

A sample of the initial material (usually from 35 to 40 mg) is lased in the ampoule and poured with the NaCl solution (a sample/solution ratio is 1/10). The ampoules were sealed and withstood at run's P-T conditions during 7 days followed by quenching of rate 100°C/min. The ampoules were gold, keeping transport of iron in/through ampoule walls. Oxygen fugacity f_{O2} was not controled, We believe that f_{O2} is closed to that of the Ni-NiO buffer [*Helz,* 1976]. When ampoules were opened, compositions of mineral phases, melts and quenched glasses, revealed in amphibolites, were investigated by a local x-ray spectral microanalysis technique using the electron scanning microscope "CamScan MV 2300" supplying with the energy dispersive spectrometer containing the semiconducting Si(Li) detector and the "INCA Energy" software. Pictures of surfaces of the samples were obtained using the secondary electron detector.

Experimental results

At T = 800-900°C, and P = 5 kbar, the chemical reaction between amphibolite ($Amph_{init}$) and H_2O or H_2O-NaCl fluids is written as: $Amph_{init} + (H_2O\text{-}NaCl) \rightarrow Amf + Gl \pm CPx \pm Pl \pm OFe + Fl$.

Amphibole (Amf) the major mineral phase, was observed in all runs quite apart from the NaCl concentration in the initial fluid. Plagioclase observed along with amphibole at 800°C had somewhat more basic composition relative to initial one ($An_{46} \rightarrow An_{50-55}$). Rare occurring clinopyroxenes are resulted from interactions of amphibolite and pure water and/or with diluted (from 1 to 5 mass % NaCl) water solutions. Increase of the NaCl concentration in the initial solution expands the field of stability for amphibole. Melt (Gl) resulting from the partial melting of amphibolite forms cement matrix between minerals. The quenched phase (Fl) precipitating from the solution is easily detected and analyzed since it present as spheres with diameters from 20 to 80-150 μm. Chemical compositions of the Gl and Fl melts (the sum of oxides is 100 mass %) resulted from the partial melting of the amphibolite at 900 °C and 5 kbar are presented in the following Table.

Table. Chemical compositions of the Gl and Fl melts (the sum of oxides is 100 mass

№ опыта	X_{NaCl} in fluid	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	NA_2O	K_2O	Cl_2O
C-14.	Without fluid	67.32	0.31	18.15	1.58	0.39	0.31	3.71	5.78	2.45	0.00
B-8	H_2O	62.10	0.10	20.72	2.81	0.35	0.04	6.64	4.51	1.83	0.00
U-1, (Fl)	0.02	64.96	0.25	22.18	1.86	0.14	0.00	4.06	5.69	0.78	0.04
S-1, (Gl)	0.10	60.06	0.36	23.74	1.79	0.08	1.00	3.37	9.04	0.31	0.36
S-1, (Fl)	0.10	60.53	0.75	24.00	1.99	0.07	0.64	3.18	8.19	0.18	0.47
S-2, (Gl)	0.25	62.36	0.50	23.66	1.09	0.06	0.35	1.31	9.91	0.06	0.70
S-2, (Fl)	0.25	61.66	0.76	24.07	1.29	0.00	0.12	1.25	10.07	0.17	0.61
S-3, (Gl)	0.50	61.96	0.54	23.75	0.98	0.00	0.39	0.81	10.32	0.08	1.18
S-3, (Fl)	0.50	62.25	0.26	23.73	1.43	0.10	0.26	1.75	8.61	0.48	1.14

As it follows from the Table, the average chemical composition of the melts is following SiO_2 – 60-62 mass %, Al_2O_3 – 23-25 %, Na_2O – 8-11%, (CaO+MgO+FeO) < 10%. All melts have quartz-norm compositions. As X_{NaCl} in the fluid increases, the melts are enriched in Al_2O_3 and Na_2O and depleted in CaO and K_2O, but their compositions remain the quartz-norm ones. Nepheline-norm melts are only formed at $X_{NaCl} > 0.5$. Concentration of Cl in the melt increases from 0.4 to 1.5 mass % with increasing X_{NaCl} in the initial fluid from 0.1 to 0.47 (Fig. 1).

The initial amphibole in amphibolite is pargasite (*Leake et al.,* 1997). After experiments, the amphiboles became strong inhomogeneous: sometimes they are zoned crystals, in which magnesium concentration increase from the centre of grains to their edges, *i.e.*, $Fe^{2+} \rightarrow Mg^{2+}$. In other cases, the magnesian edge part of amphiboles separates from its central, more ferruginous, part and fragments into very small-sized grain (Fig. 2).

It gives impression that the high-magnesian (f = 0-0.1) amphiboles dissolve gradually. Amphiboles from runs with high concentrations of NaCl (X_{NaCl}=0.78) are homogeneous, their compositions is not changed from the centre of grain to its edge. Zoning of amphiboles was observed in the experimental runs with pure H_2O as well as in those with NaCl solution. As it follows from the reaction $(Mg,Fe)_{Hbl} + H_2O \rightarrow (Mg)_{Hbl} + Fe(Sol)$, where Fe(Sol) denotes Fe complexes in the fluid as, increasing activity of water (a_{H2O}) in solution leads to the predominant leakage of Fe from mineral with respect to that of Mg. Quick quenching of the ampoules resulted in keeping the Fe^{2+} from amphiboles in fluid phase. Increase of the quenching time in two times (rate is 50°C per minute) aid considerably in crystallization of highly ferruginous amphiboles (up to f= 0.9) from fluids.

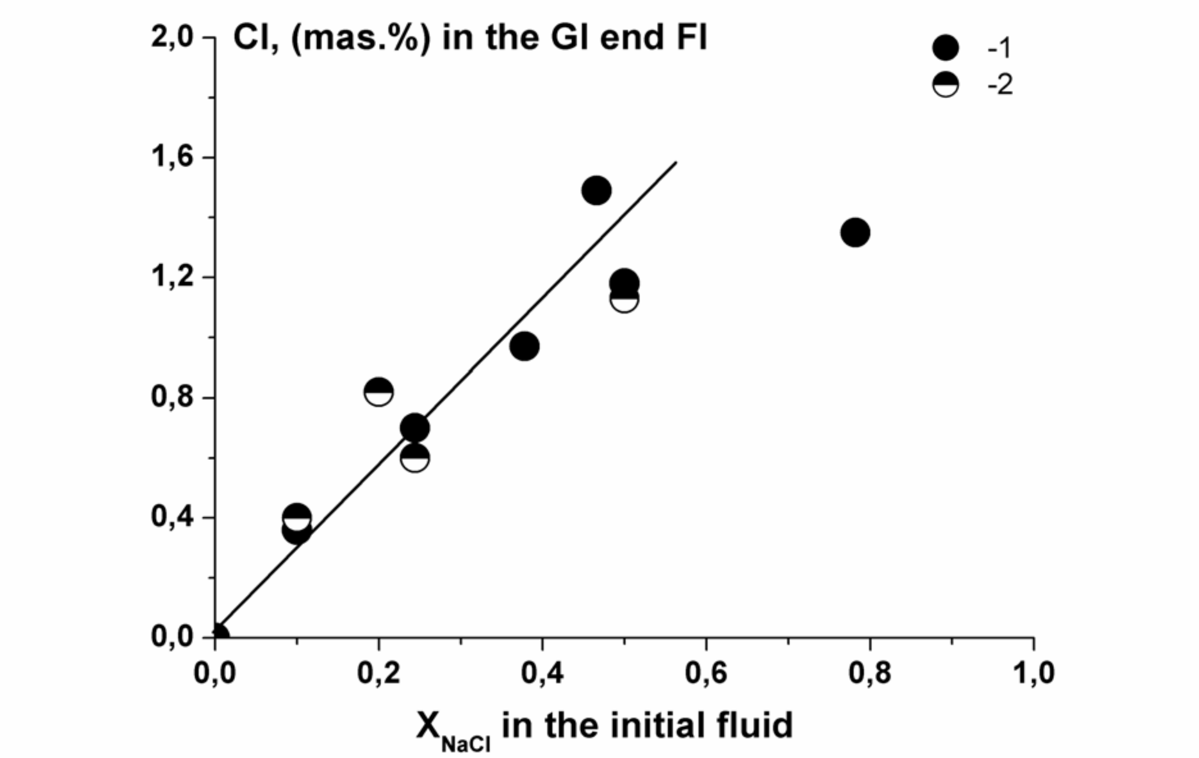

Fig. 1. Dependence of concentrations of Cl (mass %) in the melts and glasses on X_{NaCl} in the initial fluid: 1 - in the melt resulted from partial melting of amphibolite; 2 - in quenched glasses

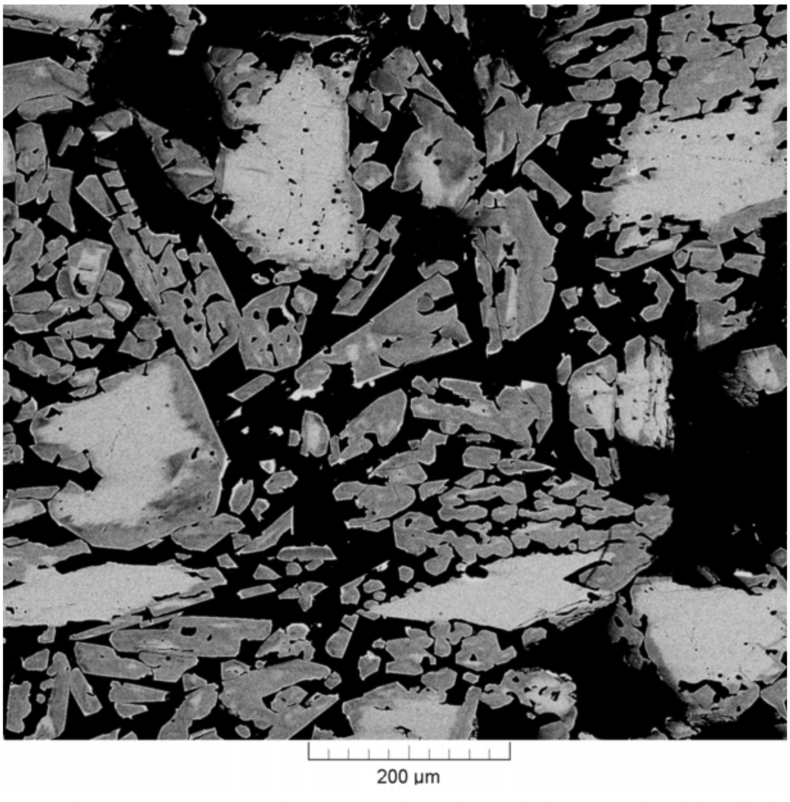

Fig. 2. Amphiboles after experiment S-1. Central parts of the mineral characterized by high X_{Fe}, whereas edge parts are high-magnesian

Another common type of isomorphic substitution in amphiboles is Ca + (Mg, Fe^{2+}) → Na + (Al, Fe^{3+}). Distribution of sums of the cations between central and edge parts of the minerals at 800 and 900°C are presented in Fig. 3.

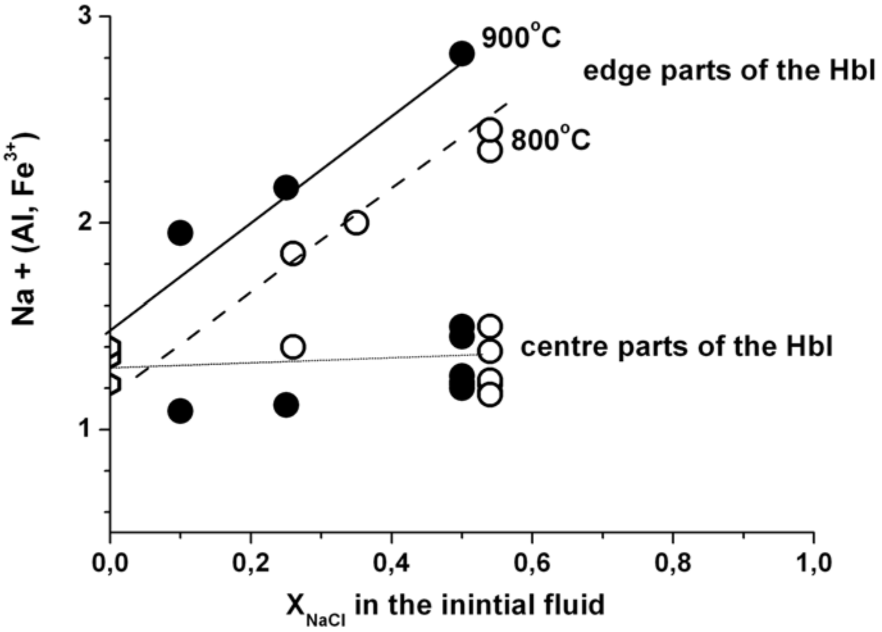

Fig 3. Relation between X_{NaCl} in fluids and ($Na+Al^{VI}+Fe^{3+}$) in amphiboles. Dark and light circles relates to 900 and 800°C, respectively

As it follows from Fig. 3, a direct correlation between the NaCl fluid concentration and concentration of Na + (Al, Fe^{3+}) in the edge zones of amphiboles is observed. Concentrations of cations in the central parts of the mineral are not changed from their initial values, because of relative short duration of the experiments. At 900°C, concentrations of (Na + (Al, Fe^{3+})) are greater than those at 800°C, because leakage of Ca + (Mg, Fe^{2+}) bases from amphibole increases with temperature.

Our experiments evidenced that

1. Partial melting of amphibolites in presence of the $NaCl-H_2O$ fluids at 900°C and $X_{NaCl} < 0.5$ results in formation of quartz-norm melts. Concentration of Cl in these melts increases from 0.4 to 1.5 mass % with increasing X_{NaCl} in the fluid phase from 0.1 to 0.47.
2. Predominant transport of Fe from amphiboles into solution with respect to that of Mg occurs in fluids with high a_{H2O} at T = 800 и 900°C. The predominant transport of Fe may be resulted from direct leakage of Fe from enclosed rocks and/or from re-precipitations of Fe-bearing minerals including X_{Fe} amphiboles. Increasing of X_{NaCl} in the fluid phase inhibits the transport of Fe from amphiboles (amphibolites).
3. Sum of cations Na + (Al, Fe^{3+}) in amphiboles is a direct function of X_{NaCl} in the fluid phase. According to preliminary data, this may be used in estimation of X_{NaCl} in the fluid phase from the chemical composition of amphibole.
4.

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