Extremely low D/H ratios of amphiboles from alkaline syenite complexes: Implications for the genesis of alkaline to peralkaline magmas or problems with mineral-water fractionations?

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The hydrogen isotope compositions measured for amphiboles from peralkaline to agpaitic rocks of the Ilimaussaq alkaline complex of Greenland are very heterogeneous and extend towards some of the most deuterium-depleted values of naturally occurring minerals (δD values between –92 and –232‰; see also Sheppard, 1986). In contrast, oxygen and neodymium isotope compositions of most minerals and rocks are quite homogeneous ($\delta^{18}O$ = 5.2 to 5.7‰; $\varepsilon_{Nd(T)}$ = –0.9 to –1.8). The δD values are also found to correlate with total Fe-contents and Fe^{3+}/Fe^{2+} ratios of the minerals. Furthermore, late-stage, primary fluid inclusions in the Ilimaussaq rocks are known to be extremely rich in CH_4 and H_2 (Konnerup-Madsen, 2001). This may lead to the suggestion that the low D/H ratios and highly reducing conditions reflect interaction with and/or assimilation of organic-rich sediments (e.g., Sheppard, 1986). However, homogeneous, mantle-like O- and Nd-isotope compositions, decreasing D/H with increasing Fe^{3+}/Fe^{2+} ratios, and δD values measured for CH_4 and H_2 from fluid inclusions (typically in equilibrium with magmatic waters; Konnerup-Madsen, 2001) argue against such a model. Instead, a complex fluid-evolution with internally-buffered fluids and late-stage re-oxidation of the previously reducing fluids during cooling may best explain the above data.

As similarly low δD values and CH_4 and H_2-rich fluid inclusions have been measured for other alkaline to peralkaline rocks elsewhere (Sheppard, 1986; Potter, 2002), such a complex fluid history may be a characteristic of undersaturated alkali- and volatile-rich melts. Alternatively, the presently known amphibole-water fractionation factors are in serious error for the Fe(tot)- and Fe^{3+}-rich amphiboles that may have formed at low pressures.

References

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Effect of temperature variations on mass transfer in fluid-rich metamorphic systems : An experimental study

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We carried out "tube-in-tube" isobaric experiments (7 kbar, Internally Heated Pressure Vessels) on two simple systems (Al_2O_3-SiO_2-H_2O and K_2O-Al_2O_3-SiO_2-H_2O), with temperature (T) varying through time. A perforated gold capsule (2 mm diameter, 15 mm long, Inner Capsule) containing ground natural minerals (quartz in excess + kyanite +/- muscovite) was placed with distillated water in a sealed gold tube (4.8 mm diameter, 35 mm long, External Tube). We conducted two experiments (increasing and decreasing T) between 350° and 550°C (steps of 20°C / day) and two isothermal experiments at 350° and 550°C. The results are shown in Table 1.

T	System	Inner Capsule	External Tube
350°C	ASH	Kaolinite	diaspore, kaolinite
	KASH	kaolinite, muscovite	diaspore, kaolinite, muscovite
550°C	ASH	kyanite, quartz	kyanite, quartz
	KASH	K-rich zeolite, muscovite, Al-rich mixed layer	Al-rich mixed layer, Muscovite
T+	ASH	Pyrophyllite	diaspore, pyrophyllite
	KASH	pyrophyllite, muscovite, K-rich zeolite	Pyrophyllite, muscovite, K-rich zeolite
T-	ASH	quartz, Al-rich mixed layer	quartz, kaolinite Al-rich mixed layer
	KASH	Quartz	quartz, kaolinite

Table 1: Experimental results. T+: increasing temperature. T-: decreasing temperature.

On its way to chemical equilibration with the starting material, the fluid gets saturated with respect to successive mineral phases which are recovered in the external tube. At a further stage, these phases can react to achieve equilibrium in the tube-in-tube system at whole. This type of crystallization in response to oversaturation, in a dynamic system, is found to be very efficient at transferring aluminum (from the inner capsule to the external tube). By analogy, Al-bearing minerals may crystallize in veins in response to T variations. In the T-varying experiments, the system developed new phases (K-rich zeolite, Al-rich mixed layer) and low-T metastable phases (pyrophyllite + diaspore instead of kyanite + quartz, kaolinite + quartz instead of pyrophyllite + quartz). Thus low-T parageneses can nucleate and be preserved in high-T conditions if the T variation through time ($\Delta T/\Delta t$) is high.