

CHLORIDE LAVAS: A POSSIBLE MAGMATIC DIFFERENTIATION PRODUCT UNDER ANHYDROUS CONDITIONS?

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The lack of water in lunar rocks, a fundamental difference from terrestrial conditions [1], leads to profound differences in magmatic behavior and evolution. Dissolved water in a silicate melt has two major effects: (1) it acts as a flux, through breaking Si-O bonds [2], and thus expedites reaction kinetics by decreasing melt viscosity. Such fluxing is extremely important in allowing late magmatic differentiates to even exist; otherwise high-silica melts are too viscous to approach equilibrium. (Experimental high-silica systems are run "wet" for this reason [3].) (2) Water is concentrated into the residual melt during magma fractionation, where it eventually exsolves as a separate vapor phase into which many incompatible elements partition [4]. This exsolved phase is the source of a classic hydrothermal deposit, a traditional source of economic mineralization [5].

Although the Moon is turning out to have a more complex and protracted igneous history than had initially been thought [6], it nonetheless is still generally considered that, because of its waterlessness, the Moon has had much simpler magmatic evolution. However, extremely differentiated indigenous igneous rocks occur on the Moon; not merely KREEP material, but "granites" (highly differentiated rocks containing free silica and alkali feldspar) as well. Their origin remains controversial [7], but they may be much more common than previously supposed [8].

Given the existence of such highly differentiated rocks, it is worth further investigating the possible evolution of anhydrous magmatic systems. If no other fluxing agents exist, the result in a high-silica system will presumably be glass. Laboratory considerations suggest, however, that other fluxes, such as F, Li [9], or B [10], can work in the absence of water. Fluoride has, of course, been used as a flux in glassmaking for centuries [11]; it also breaks silicate polymerization [12]. Moreover, these elements are incompatible and also tend to become concentrated in the residual melt. Thus, if melt viscosity is low enough, other incompatible elements will also be free to concentrate into the late-stage melt, and the question then is the behavior of such incompatibles as cooling continues, as no water-rich vapor phase into which they can partition will exsolve.

Unmixing of a chloride-rich liquid is a possibility suggested by experiments in the NaCl-albite system [13]. Other incompatible elements may well partition into such a chloride liquid; furthermore, NaCl and KCl have a eutectic at 658° C, and the melting point decreases even more with additional components such as LiF [14]. (By contrast, fluoride is much more soluble in a silicate melt, probably because of the similar size of F⁻ and O²⁻. NaF and albite are miscible [15], although glassmaking experience indicates that fluoride salts exsolve from certain other silicate systems [16].)

Magma generation by salt unmixing is not unheard of; carbonatites probably result from unmixing of alkali carbonates from alkali silicates [17]. As for carbonatites, separation of the immiscible salt liquid may be expedited because a chloride melt will remain fluid at much lower temperatures than the silicate host. Indeed, contact metamorphic reactions with solid country rock, to produce minerals such as sodalite and scapolite, may produce a distinctive reaction rime.

This speculated mechanism has obvious potential relevance to the Moon. Although all volatiles, including halogens, are depleted, the halogens are still present in significant amounts, in contrast to H. One possible complication, however, is that phosphate may act as a halogen scavenger, to the point that commonly no chlorine remains in late-stage melts. Chlorofluorapatite is a common accessory on the Moon, and seems to form until the halogens are exhausted [18], after which the anhydrous calcium phosphate "whitlockite" [19] forms instead, because without water hydroxyapatite cannot form.

Chloride magmas are totally speculative at this point, and even if they once existed, the deposits they left will be extremely rare. However, they are a possibility that could be specifically

sought in further lunar exploration. Such deposits might also have possible economic significance as a source of rare elements for lunar and near-Earth space operations.

Last, the general mechanism of chloride magma generation is possibly relevant to other waterless planets such as Mercury and Venus. The latter in particular is a large planet with a great deal of internal heat production, and thus presumably has had much more protracted and extensive igneous activity than the Moon. This could favor the generation of chloride magmas, particularly if some sort of crustal recycling takes place so that multiple fractionations can occur. Chloride eruptions may perform a minor but interesting role, like (say) fumarolic activity on Earth.

Laboratory work to further determine behavior in anhydrous systems would obviously be useful; e.g., the compositions and temperatures in silicate-halide systems at which halides exsolve, and the partitioning of elements into molten salt. Before any experimental program is begun, however, it should be noted that much industrial and chemical literature, not previously relevant to natural systems, may be useful; molten salts as solvent systems in particular have an extensive literature [20]. Other further work could focus on the possible signatures of chloride-rich units that could be detected with remote sensing or in regolith samples. Such deposits may be difficult to recognize because chlorides will be relatively volatile at the lunar surface.

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