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EXPERIMENTAL STUDY OF CHEMICAL, PHASE AND TEXTURAL EQUILIBRIUM OF HIGH TiO_2 MARE BASALTS AND PERIDOTITE

Brief summary of entire project

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SUMMARY OF RESEARCH PROJECT

I. Basalt Petrogenesis

We continue to explore the interrelations between the dynamics of melting and melt segregation with the large scale convection within planetary mantles (Hess, 1993; Hess and Parmentier, 1993; Parmentier et al., 1993, Parmentier and Hess1992a,b). We have also completed a series of experiments to measure the dissolution rates of anorthite and the chemical diffusivities of Al in haplo-picrite mare basalts (Finnila et al., 1994, 1993, 1992) and have applied these results to model the processes of assimilation of anorthositic lunar crust into picrite-mare basalts (Finnila et al, 1994) and the Mg*-rich suite parent magmas (Hess, In press; Hess, 1992). Experiments are in progress to determine the solidus of ilmenite-bearing peridotites and the liquidus of ilmenite in picrite mare liquids at appropriate ranges of pressure and temperature (Hess, 1993). These data will be applied to constrain the depths of the high-Ti picrite source regions and hence, address the thermal, chemical and temporal evolution of the lunar interior.

In Hess (1993), I used the compositions of three ilmenite saturated Apollo 15 Red Glasses from Delano (1980) and volumetric data for ilmenite and the normative liquid component $FeTiO_3$ to calculate the ilmenite liquidus in high TiO_2 mare glasses over a range of pressures and temperatures appropriate to the lunar mantle. After estimating the P-T coordinates of the ilmenite-peridotite solidus, I argued that the range of compositions of mare picrite glasses from Delano (1986) are consistent with a mantle source that contained low CaO-pyroxene ± olivine. Since the high TiO_2 mare picrite glasses have low CaO-pyroxene on the liquidus at pressures greater than 2.0 GPa (Green et al, 1975; Delano, 1980; Wagner and Grove, 1993), it follows that the mean depth of magma generation (Longhi, 1992;1993) is greater than 2.0 GPa provided that the glasses are near primary or at least primitive melts. If this analyses is correct, it requires that ilmenite-bearing cumulates exist even in the lowermost portions of the lunar mantle, implying that the cumulate pile of the magma ocean became gravitationally unstable and dispersed late-stage ilmenite-enriched layers throughout the moon.

The cumulate-overturn model is highly controversial and not yet proven. Nevertheless, Hess and Parmentier (1993) applied boundary-layer theory to examine whether the gravitational forces are sufficient to initiate

Hess (In press, 1992) has considered the petrogenesis of the Mg-rich suite and particularly, the very primitive Mg-troctolites. Of the various models considered, the most likely origin of the troctolite parent magma is by the melting of a primitive moon of Mg* ≥88, perhaps followed by slight reduction of FeO to Fe metal. Alternatively, the parent magmas may be impact melts of anorthositic crust and the Mg*-rich dunite cumulates of the magma ocean. This latter model faces some difficulties but cannot be totally discounted (see also Taylor et al., 1993).

Instabilities within planetary mantles can provide novel and unusual constraints on igneous petrogenesis. Indeed, plate tectonics provides a vital framework for volcanic activity on Earth, and cumulate-overturn and remelting of the disturbed lunar interior may be one of the critical components in theories of igneous petrogenesis on the Moon. Similarly, Parmentier and Hess (1993, 1992) and Hess (1991) have argued that the absence of terrestrial-like plate tectonics on Venus places unique boundary conditions on the igneous evolution of the planet.

Partial melting of the Venusian mantle to generate basaltic crust must inevitably leave behind a compositionally buoyant but relatively refractory mantle. In the absence of plate tectonics on Venus, this buoyant layer collects on top of the mantle and acts as a thermal insulator, causing the interior of the planet to heat up. The development of thermal buoyancy of the Venusian interior coupled with the conductive cooling of the upper depleted mantle ultimately leads to an instability which sweeps a portion of the upper mantle and crust back into the mantle. Upwelling of fertile and hot mantle leads to extensive melting and volcanic resurfacing.

One dimensional parameterized convection models find that such instabilities are periodic and lead to the volcanic resurfacing of the planet with periods of 300 to 500 my (Parmentier and Hess, 1992). These processes may account for the mean surface age of about 500 my, the small number of volcanically modified impact craters (Schaber et al., 1992), the large apparent depths of compensation, the absence of a low viscosity layer (Smrekar and Phillips, 1991) and the eruption of voluminous, high temperature, possibly komatiitic magmas (Hess and Head, 1990). Nevertheless, the model must be examined and tested more fully to understand the mechanisms of crustal recycling on Venus.

II. Petrogenesis of Highly Evolved Magmas

This research is concerned with the origin and evolution of KREEP-enriched basalt, and particularly with important points in the liquid lines of descent which mark the incoming of ilmenite, whitlockite, apatite and SiO_2-enriched melts, immiscible or otherwise. We demonstrated that the liquid line of descent of Apollo 15 KEEP basalt 15386 was characterized first by the crystallization of plagioclase and low CaO pyroxene, producing a ferrobasalt with little to not SiO_2 enrichment (Hess et al., 1989;). After about 60% crystallization of these phases, ilmenite appeared on the liquidus. The crystal-liquid bulk distribution coefficient for SiO_2 was reduced to values less than unity, causing the SiO_2 content of the residual liquids to increase to more than 55 wt %. The liquids at this point match the QMD 15405 composition very closely, indicating that some quartz monzodiorite compositions were indeed liquids produced by extended crystal fractionation of KREEP basalts, as argued by Ryder (1976). With continued fractionation, whitlockite appears at P_2O_5 contents of about 2.5% and 1050-1025°C, and then the QMD liquids become immiscible, producing coexisting lunar granites and ferrobasalts (Hess and Rutherford, 1989; Hess, 1988). The liquid line of descent of 15386 is composed of 3 segments: (1) a tholeiite trend of FeO enrichment without concomitant SiO_2 enrichment; (2) a SiO_2 enrichment trend heralded by the appearance of ilmenite; and (3) the onset of whitlockite saturation prior to the development of liquid immiscibility.

The crystallization of whitlockite occurs in mare and non-mare basalts only after large degrees of crystal fractionation of the parent liquid-e.g., after about 60% crystallization of 15386. This is in line with the observation that only lunar granites show a REE signature of phosphate fractionation and whitlockite/apatite apparently have not fractionated from KREEP-enriched parent magmas. Thus, KREEP liquids are saturated with ilmenite but not with phosphates. It is surprising, therefore, that REE-rich phosphates, whitlockite and apatite, occur together in relatively rich Mg-rich highland lithologies, including alkali and magnesian anorthosites, troctolites and gabronorites (e.g., Warren et al., 1983). The whitlockites typically are magnesian ($Mg^* \geq 60$), whereas apatites are ferroan ($Mg^* \leq 40$). The whitlockites, paradoxically, have REE contents that are 20 to 30 times the REE contents of nearby apatite (e.g., James et al., 1987). Some authors argue from these apparent contradictions that the phosphates were introduced by one or more metasomatic fluids. Others appeal to unusual phosphorous-rich but Mg*-rich parent liquids.

Neither model is required to explain the coexistence of whitlockite and apatite in the mesostasis of mare and non-mare basalts, eucrites, SNC meteorites and even some lunar granites. In all cases, the REE content of whitlockite is many times that of the apatite, and the Mg* of whitlockite is much higher than in apatite. It appears that crystal-liquid effects in derivative liquids developed from "normal" lunar primitive basalts are capable of duplicating the characteristics of phosphates observed in the highland suite lithologies.

In order to resolve some of these questions, we first determined the saturation surface of whitlockite by adding adequate quantities of $CaHPO_4$ to liquids obtained along the liquid line of descent for 15386, and equilibrating these at various temperatures. These results, and additional data obtained in other studies (primarily two liquids coexisting with whitlockite) are mapped into P_2O_5-SiO_2-temperature. As expected, the P_2O_5 content of whitlockite saturated liquids varies inversely with SiO_2 content and directly with temperature. A QMD liquid with about 55% SiO_2, for example, is saturated with whitlockite at 1050° and about 2.5% P_2O_5. A granite liquid, however, requires less than 0.5% P_2O_5 at 1000°C, whereas a coexisting immiscible ferrobasalt may require 4% P_2O_5.

FeO/MgO whitlockite/liquid distribution coefficients are less than unity, meaning that whitlockites are considerably more Mg* rich than the coexisting melt. In fact, in melts with low MgO, whitlockites have higher Mg* ratios than coexisting olivine and/or pyroxene. The high Mg* values of whitlockite in the highland lithologies, therefore, does not require a primitive parent liquid. Additional experiments over a wider range of temperatures and liquids are being run to constrain these results more precisely.

Apatite-liquid FeO/MgO distribution coefficients in similar liquids have not been obtained yet. This is our next project. A few apatite/basanite distribution coefficients, however, were obtained by Watson and Green (1981), and are close to unity. If these data are representative for a wider range of liquids and temperatures, they indicate that the (FeO/MgO) apatite/whitlockite distribution is significantly greater than one. The high Mg* values of whitlockite and the comparatively low Mg* values of nearby apatite in lunar igneous rocks are therefore compatible with the relations observed in our experiments.

The extraordinarily high REE contents of whilockite are not as easily explained. The REE contents of whitlockite reach values over 30,000 times chondrite, whereas adjacent apatites have REE contents of only about 1,000 times chondrite (James, et al., 1987). Yet, the REE partitioning coefficients obtained by experiment (Dickinson and Hess, 1983; Watson and Green, 1981) for whitlockite/apatite are close to unity. If these distribution coefficients are accepted uncritically, it is required that whitlockite and apatite crystallized from liquids with chondrite normalized REE values of 3000-5000 and 100-150 respectively. There is no simple petrogenetic mechanism to rationalize these results.

The paradox is resolved, if only partially, if we question the experimental REE distribution data for whitlockite/liquid. Hess (oral presentation at Lunar & Plan. Sci. Conf. XXI) argued that the REE enter whitlockite in a coupled substitution

$$2\,^{[8]}\mathrm{Ca} + 1\,^{[6]}\mathrm{Ca} = 2\,^{[8]}\mathrm{REE} + \mathrm{VAC}$$

where a "special" octahedrally coordinated Ca site (Dowty, 1977) becomes vacant and the REE are partitioned into the 8 coordinated Ca site. The solubility of REE is therefore limited by the number of "special" Ca sites. High REE contents are used in the partitioning experiments, which saturated the REE sites in whitlockites. The REE distribution coefficients reflected the high REE contents and were not necessarily appropriate for liquids with more normal REE values. Much higher whitlockite/liquid REE distribution coefficients were predicted at lower REE contents. McKay et al., (1987) found that the whitlockite/liquid REE distribution coefficient did indeed increase by a factor of 3 as the REE contents were decreased. Additional experiments in QMD compositions are required to test these ideas and to model the origin of whitloockite/apatite assemblages more accurately. The preliminary results discussed above indicate that their paragenesis does not require unique magmas or metasomatic processes, however.

III. E Chondrites

Enstatite chondrites and achondrites are the only meteorite classes with significant Si in solid solution in kamacite. Any petrogenetic model must deal with this fact and with the apparent systematic variation of the Si content of E chondrite groups. The Si content of kamacite clearly distinguishes the EH chondrites (>.044 mol % Si) from the EL chondrites (<.035 mol % Si) (Keil, 1968; Sears, 1980; Rambaldi et al., 1984). Moreover, the Si contents vary with petrological classification. The EH3 and EH3-4 groups (Qingzhen, ALHA 77156, Kota-Kota, Parsa) have lower Si contents (.04-.05 mol %) than the EH4 and EH5 groups (>.05 mol %) (Abee, Adhi-Kot, Indarch, South Oman, Saint Savier, St. Mark).

The data cannot reflect solely a condensation history. Sears (1980), for example, showed that the equilibrium, kamacite-enstatite-gas, produced metal of progressively lower Si contents at lower temperatures of equilibration. However, Larimer and Buseck (1974) found that the Si-content of kamacite in an assemblage with enstatite-quartz-pyrrhotite-oldhamite decreased with increased annealing temperatures. Thus, the Si contents probably reflect both nebular and planetary processes. We have repeated the Larimer-Buseck calculation using updated thermodynamic data and the activity coefficients of Si in metal from Sakao and Elliot (1974). The two modifications each produce changes of more than 100°C in the "equilibrium" temperatures although these changes are in opposite directions and partially offsetting (Fogel et al., 1989). In any case, the "equilibrium" temperatures are not simply correlated with metamorphic grade: one of the highest temperature is obtained for Indarch, an EH4 chondrite, and the lowest for the two EH5 chondrites. The source of these discrepancies lies either with the thermodynamic data and solution models (a factor of 2 uncertainty in the $\gamma CaSiO_3$ in pyroxene yields ±50°C uncertainty in the temperature) and/or with the kinetics of these reactions in the chondrites themselves. The latter possibility suggests that the metamorphic temperatures which have been calculated are minima (Larimer and Buseck, 1974). However, this suggestion is in conflict with the findings of Herndon and Rudee (1978) who conclude that Abee, metamorphic temperature 542°C, cooled through 700°C in less than 10 hours! The low metamorphic temperatures St. Sauveur and St. Marks are also inconsistent with the data of Skinner and Luce (1971) who find that these meteorites must have cooled past

800°C in less than six hours! Clearly, there are some serious problems with these calculated temperatures.

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