SUBSOLIDUS REDUCTION OF LUNAR OPAQUE OXIDES: EVIDENCE, ASSEMBLAGES, GEOCHEMICAL RELEVANCE, AND EVIDENCE FOR A LATE STAGE REDUCING GASEOUS MIXTURE, A. El Goresy, and Paul Ramdohr, Max-Planck-Institut für Kernphysik, 69 Heidelberg, Germany

Lunar basalts differ from terrestrial counterparts mainly in their extremely low oxygen fugacities. The opaque oxide minerals in lunar rocks from various landing sites display textures indicative of subsolidus reduction. Very probably many of the lunar magmas were already in a reduced state at the time of extrusion (Sato et al. 1973). The intensity of the reduction as documented by a number of reactions compared to buffer curves of the system Fe-FeO-TiO_2 (Sato et al. 1973) vary among rocks of different landing sites. Considerable variation in the intensity of reduction was also reported among rocks of the same landing site (El Goresy et al. 1972; Haggerty 1972). Six subsolidus reduction reactions, which can be applied for estimation of the degree of reduction, were observed in lunar rocks (El Goresy et al. 1972; Haggerty 1972, 1973; Sato et al. 1973; Mao et al. 1974): 1) Ulvöspinel \( \rightarrow \) ilmenite+Fe+O; 2) ilmenite \( \rightarrow \) TiO_2+spinel+Fe+O; 3) ilmenite \( \rightarrow \) armalcolite+Fe+O; 4) armalcolite \( \rightarrow \) TiO_2+Fe+O; 5) fayalite \( \rightarrow \) Fe+SiO_2+O; 6) rutile \( \rightarrow \) TiO_1-x (blue rutile)+xO (this work). Of these six reactions reactions 3 and 4 were only observed in rocks subjected to intense heating and reduction during events in the lunar regolith involving solar wind hydrogen. Reaction 1 takes place in two stages depending on the intensity of the reduction and the prevailing temperature. The first stage is characterized by two distinct assemblages: a. Cr-ulvöspinel+ilmenite and b. Cr-ulvöspinel+ilmenite+Fe (Haggerty 1972; El Goresy et al. 1972). In the second stage extensive subsolidus reduction reveals the assemblage Al-Ti-chromite+ilmenite+Fe. The first stage was reported from numerous basalts of every landing site, whereas the second stage was only observed in rocks 14053, 14072 (Fra Mauro) and few TiO_2 rich basalts from the Taurus-Littrow region. In rock 14053 the reduction of chromian ulvöspinel to Al-Ti-chromite+ilmenite+Fe is accompanied by the decomposition of fayalite to Fe+SiO_2. This is interpreted as indicative of intense reduction of this sample. Although ilmenites in 14053 show partial rather than pervasive breakdown to rutile+Fe, they were found to contain Ti^3+ (Pavitević et al. 1972). Based on experimental investigations Taylor et al. (1972) interpret these textures as due to the more slow breakdown of ilmenite to rutile+Fe subsequent to the ulvöspinel breakdown. In contrast, sample 70035, and 70135 from Taurus-Littrow site display extensive subsolidus reduction of ilmenite to rutile+spinel+Fe and many of the rutiles show indications of reduction to oxygen deficient blue rutile. Subsolidus reduction of ulvöspinel is, however, not as pervasive as in samples 14053 and 14072. The mechanism of subsequent reduction reactions as proposed by Taylor et al. is not compatible with these features. Very probably the rocks of the two landing sites had different thermal histories.

We propose the following alternative to explain the different subsolidus reduction reactions observed in samples 14053 and 14072 on one side and samples 70035, and 70135 on the other hand: Samples 14053 and 14072 were subjected to intense reduction upon heating to a temperature close to 950°C. At this temperature the Fa/Q+I buffer curve intersects the U/Il+I buffer curve. Reduction upon heating close to that temperature at the given oxygen fugacity
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reveals simultaneous breakdown of fayalite to Fe+SiO₂ and ulvöspinel to ilmenite+Fe. Incipient breakdown of ilmenite to rutile+Fe may indicate that either the 1) opaque assemblage was indeed placed below the I1/Ru+I fugacity curve at or close to 950°C to account for extensive subsolidus reduction of both fayalite and chromian ulvöspinel followed by rapid cooling thus preventing further ilmenite breakdown, or 2) the reduction of 14053 at 950°C was not intense enough perhaps just at the I1/Ru+I buffer curve. This would require that the temperature was held for prolonged times under the same reducing conditions to allow extensive breakdown of fayalite and ulvöspinel. We are in favor of the first alternative for the following reasons. Extensive studies of pigeonites from 14053 (Finger et al.1972) indicate that the original cooling rate of this rock was quite slow.After solidification and cooling to low temperatures the rock was reheated to a peak temperature in excess of 840°C followed by extreme rapid cooling. Samples 70035, and 70135 display breakdown textures of ulvöspinel to Al-Ti chromite+ilmenite+Fe and ilmenite to rutile+spinel+Fe, but no breakdown of fayalite was observed. The reduction took place above the Pa/φ/I curve but below the I1/Ru+I buffer curve. In contrast to 14053 and 14072 samples 70035, and 70135 were reduced at much lower temperatures and upon cooling. The reduction phenomenon is not unique to the Apollo 17 basalts but is also present in numerous Apollo 11, Apollo 12 and Apollo 15 igneous rocks (Simpson and Bowie 1970; El Goresy et al.1971, 1972; Haggerty 1972).

What was the nature of the reducing phase? Extensive studies in reflected light, with the scanning electron microscope, and with the electron microprobe indicate that after solidification of the basalts metallic iron deposited due to the breakdown of a gaseous mixture which have permeated the rocks thus leaving a network of iron veins across silicates and oxides. Especially along such veins breakdown reactions were found to be pervasive indicating that a single event is probably responsible for both reduction and iron precipitation. Additional evidence was also found for reaction between sulfur bearing vapors and ilmenite thus depositing troilite+spinel+rutile. Very probably after cooling to moderate temperatures indigenous gas mixtures released from the lunar magma permeated these rocks. An excellent candidate as a member of such gas mixture is iron carbonyl which breaks down upon cooling to iron +CO. Carbon monoxide released would account for extensive reduction of the opaque assemblages.

References
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HALFTONES - NOT PRINTED

Fig. 1a  Fig. 1b
Scanning electron microscope pictures of sample 70035,16 showing metallic iron (white) deposited from a vapor phase in cleavage of pigeonite (Fig. 1a) and in a crack in ilmenite (Fig. 1b).