CRYSTAL CHEMICAL CONTROL OF ELEMENT PARTITIONING FOR COEXISTING PIGEONITE-AUGITE AND CHROMITE-ULVÖSPINEL, Hiroshi Takeda[1,2], Masamichi Miyamoto[2] and Arch M. Reid[1] ([1]NASA Johnson Space Center, Houston, TX 77058 and [2]Mineralogical Institute, Faculty of Science, Univ. of Tokyo, Hongo, Tokyo 113 Japan)

In attempts to decipher the petrogenetic evolution of lunar basalts the partitioning of major and trace elements among coexisting minerals has been extensively studied (e.g. 1,2). The effects of crystal chemical control over partitioning are extremely significant but commonly are not studied in detail. This paper presents crystallographic and chemical data on partitioning between two coexisting mineral pairs where crystal chemical control can be clearly delineated. The crystal structures of host pigeonite and exsolved augite from KREEP basalt 14310,90, and of core chromite and rim ulvöspinel from mare basalt 12052,109, have been refined by least-squares techniques using x-ray intensities measured with a single crystal diffractometer. Crystal chemical data on the pigeonite and augite from 12052 (3), the olivine from 12052 (4) and the orthopyroxene from 14310 (5), have already been published. Refinements were made employing a new program system, MINEPAC, developed by TSS on a HITAC 3800/8700 system at the University of Tokyo.

Pigeonite-augite in 14310.

The pink to brownish intermediate pigeonite from 14310,90 has augite exsolution lamellae on (001) that are coarse enough to obtain microprobe analyses (Table 1). Within these chemical constraints the cation distribution in the M1 and M2 sites and the atomic parameters of host pigeonite and exsolved augite, have been refined using 880 (pigeonite) and 340 (augite) non-overlapping reflections. Preliminary least-squares refinements resulted in R-values of 0.049 and 0.056 respectively. The methods of intensity measurement and refinement are given by Takeda (3).

Site populations and mean M-O bond distances for the pigeonite are M1 (0.56 Mg+0.43 Fe), 2.103Å; M2 (0.21 Mg+0.68 Fe+0.11 Ca), 2.091 (O1,2) and 2.517 (O3) Å and for the augite are M1 (0.64 Mg+0.36 Fe) 2.090 Å; M2 (0.16 Fe+0.84 Ca) 2.307 (O1,2) 2.686 (O3) Å. The smaller M1 size in the augite is partly due to the presence of Al. Thus Mg-Fe partitioning between pigeonite and augite may have taken place essentially between the pigeonite M2 site and the pigeonite and augite M1 sites. The site preference of Fe for the M2 site on slow cooling may then be a major reason for Fe-enrichment in the host pigeonite.

Table 1. Cell dimensions and chemical compositions of bulk pigeonite, pigeonite host and augite lamellae from sample 14310,90.

Cell Dimensions	a	b	c	β
Host pigeonite	9.715(1)	8.963(1)	5.239(1)	108.64(2)
Augite lamellae	9.713(2)	8.964(2)	5.266(2)	105.93(2)

Cations per 6 oxygens	Si	Al	Ti	Fe	Mg	Ca	Mn
Bulk pigeonite	1.984	0.025	0.021	0.941	0.731	0.278	0.002
Host pigeonite	1.993	0.012	0.015	1.092	0.767	0.106	0.001
Augite lamellae	1.946	0.061	0.033	0.541	0.633	0.773	0.004

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Chromite-Ulvöspinel in 12052.

Octahedral crystals of spinel in a vug from rock 12052,109 consist of chromite cores overgrown by and sharing crystallographic axes with ulvöspinel. One of the chromite crystals (C1) has virtually no rim of ulvöspinel whereas the other crystal studied (C2) has a thick ulvöspinel rim (U2). Chemical and crystallographic data on these spinels and on a pink spinel (chromian pleonaste, FMSP2) from an Apollo 14 breccia (14321), are presented in Table 2. Diffraction intensities were measured with a 4-circle single crystal diffractometer, using Mokα radiation with a graphite monochromator and a scintillation detector. Data were corrected for Lp factors and for absorption and reduced to structure factors. Overlapping reflections with 2θ angles less than 39° for the C2-U2 crystal were not used in the refinements. Site occupancy factors, u-parameters and anisotropic temperature factors were refined by least-squares (Table 3).

The site-occupancy refinements indicate that Cr^{3+} and Ti^{4+} show a strong preference for the octahedral site (B-site), and Fe^{2+} for the tetrahedral site (A-site). These site preferences are in accord with crystal field theory predictions (6,7). The Mg-Al substitution was considered but refinements were unsuccessful as the difference in scattering factors is not large enough to be distinguished within the accuracy of our intensity measurements. The results indicate that the possibility of partial Mg-Al disorder cannot be ruled out.

The bond distances are compatible with the refined site occupancies (Table 2). In chromian pleonaste the A-O distance is significantly larger than the B-O distance. The majority of the Mg must thus be present in the A-site since, for the oxygen positions (u=0.375) in an ideal structure with the closest packing of oxygens, A-O is 1.757Å and B-O is 2.029 Å.

We note that each of the A-O and B-O distances in both titanium chromite and chromian ulvöspinel are nearly identical. This similarity in size indicates that, at least as far as crystal chemical data are concerned, there may be continuous solid solution between chromite and ulvöspinel. However, in titanian chromite A-O is slightly larger than B-O whereas the reverse relationship holds in chromian ulvöspinel. The size difference can be attributed to the presence of minor Al in the B-site, consistent with the high correlation between (Cr^{3+}+Al) and Ti^{4+}(8). The size difference should become significant where substantial amounts of Al are present in the B site supporting the concept of an immiscibility gap in the Al-rich portion of the solid solution series.

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Table 2. Cell dimensions and chemical compositions of core chromite and rim ulvöspinel from sample 12052, and of chromian pleonaste from an Apollo 14 breccia.

	Cell Dimension	Cations per 4 oxygens						
	a	Al	Ti	Cr	Fe	Mg	Ca	Mn
Chromite	8.3314 (7)	0.481	0.120	1.259	0.783	0.357	0.001	0.009
Ulvospinel (a)	8.479 (5)	0.109	0.829	0.207	1.839	0.017	0.000	0.013
Pleonaste	8.114 (8)	1.846	0.005	0.143	0.166	0.841	0.000	0.000

Table 3. U-parameters, site occupancy factors and bond distances for chromite (C1) and ulvospinel (U2) (12052) and chromian pleonaste (FMSP2).

	C1	U2	FMSP2		C1	U2	FMSP2
Oxygen			No. of Refl.		59	50	72
u-param.	0.3879(3)	0.3868(6)	0.3888(3)	R	0.028	0.056	0.044
	Tetrahedral site (A)				Octahedral site (B)		
Mg	0.33	0.02	0.84		0.01[d]	0.0	(0.03)[a]
Fe	0.67	0.98	0.16		0.06[d]	0.43	(0.02)[b]
Al	0.0	0.0	(0.06)[a]		0.24	0.05	0.92
Cr	0.0	0.0[b]	(0.03)[b]		0.63	0.11	0.07
Ti	0.0	0.0[c]	0.0		0.06	0.41	0.005
(A,B)-O,Å	1.989(4)	2.010 (8)	1.952(4)		1.981(2)	2.024(4)	1.923(3)

a,b,c and d are maximum values when Mg/Al, Fe/Cr, Fe/Ti and Fe/Mg were varied together, respectively.