RAMAN SPECTROSCOPIC CHARACTERIZATION OF THE FELDSPARS – IMPLICATIONS FOR *IN SITU* SURFACE MINERAL CHARACTERIZATION IN PLANETARY EXPLORATION.

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Introduction: The availability in the last decade of improved Raman instrumentation using small, stable, intense lasers, sensitive CCD array detectors, and advanced fast grating systems enabled us to develop the Mars Microbeam Raman Spectrometer (MMRS), a field-portable Raman spectrometer with precision and accuracy capable of identifying minerals and their different compositions [1]. For example, we can determine Mg cation ratios in pyroxenes and olivines to ±0.1 on the basis of Raman peak positions [2,3]. Feldspar is another major mineral formed in igneous systems whose characterization is important for determining rock petrogenesis and alteration. From their Raman spectral pattern, feldspars can be readily distinguished from ortho- and chain-silicates and from other tecto-silicates such as quartz and zeolites [e.g., 4]. We show here how well Raman spectral analysis can distinguish among members within the feldspar group.
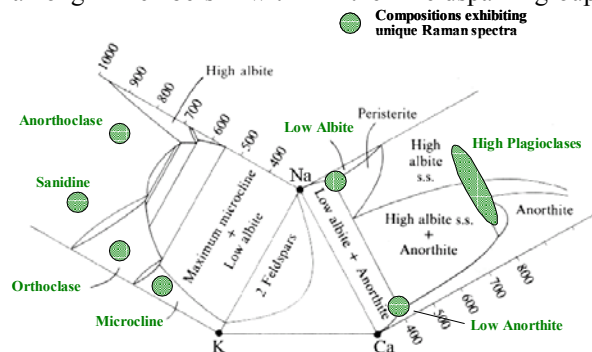

Figure 1. Generalized Feldspar Ternary phase diagram (after Zoltai and Stout [6]) with the studied samples shown in green.

Feldspars are anhydrous aluminosilicates consisting of corner-sharing $(Al, Si)O_4$ tetrahedra. These tetrahedra are arranged around polyhedral sites that contain charge-balancing cations, mainly Na^+, K^+, and Ca^{++} [5-6]. Naturally occurring feldspars form a K-Na join (miscible at high temperature) and a Na-Ca join (miscible at most temperatures, but showing intergrowths under other conditions) in a ternary system (Fig.1). Cation ratio and Al-Si ordering among tetrahedral sites provide constraints on chemical compositions of magmas and temperatures/rates of crystallization.

Numerous studies have been made of Raman spectra of naturally occurring and synthetic feldspars and glasses [7-17]. These papers, however, focus mainly on single subsets of feldspars. Thus, attempts based on existing literature to find correlations between Raman spectral features and feldspar structure and chemistry are hindered by variations in sensitivity, spectral reso-

lution, and wavelength calibration of earlier Raman instruments. To provide a better correlation, we analyzed feldspar samples using a single modern laboratory spectrometer to eliminate systematic differences in calibration.
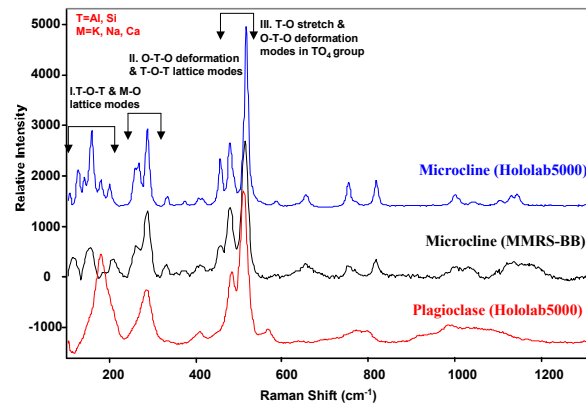

Figure 2. Raman Spectra of Typical Feldspars.

Experiments and Results: We have acquired Raman spectra of 20 feldspar samples of known Na-K-Ca compositions and Al-Si ordering (Fig.1) using a Kaiser Optical Hololab 5000 Raman system fitted with a 532 nm solid state laser for excitation. Raman spectra typical of feldspar are shown in Fig. 2. The microcline spectrum obtained with the Hololab is compared with a spectrum of the same sample obtained with the advanced brassboard of the MMRS [1]. Spectra of plagioclase and microcline differ in numbers of peaks, peak positions, and peak widths.

Raman spectra of feldspars show three spectral regions containing relatively strong peaks (labeled I, II, and III in Fig.2). These regions were assigned by von Manfried and von Stengel [7] on the basis of their predominant vibrational modes, obtained using GF force field calculations. A review of our Raman data plus the Raman spectra of some 20 other feldspar samples described in the literature [7-17] shows that seven types of feldspars, differing in cation composition or degree of Al-Si ordering (Fig. 1 and Table I), can be distinguished from each other on the basis their Raman spectral features, provided that the Raman instrument is calibrated to within ±1.0 cm⁻¹.

Three end-members of low temperature feldspars (microcline, albite, and anorthite) are distinguished from each other and from the other feldspar types by the multiplicity of the Region III Raman peaks and the

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location of the strongest peak in this region above 500 cm^{-1}.

Alkali feldspars on the K-Na join (K/(Na+K) $\geq$ 0.6) have their strongest Region III Raman line in the narrow range of 512.5 to 514 cm^{-1}, distinctly higher than the corresponding peak from plagioclases. The cation substitution also causes the spectral pattern to change from a triplet to a doublet in Region III, broadening of major peaks, and a shift of the major peak positions in Region I to higher wavenuembers.

Potassic end-member alkali feldspars crystallized at high temperatures (orthoclase & sanidine) lack spectral details of their low-T counterparts and show peak broadening but retain the triplet pattern in Region III. Orthoclase and sanidine are distinguished from each other by the peak positions of the Regions I and II lattice modes, as well as by peak widths.

The high-temperature plagioclases (Na-Ca join) also lack minor spectral peaks and have relatively broad major peaks in Regions I, II, and III. For plagioclases with >10% anorthite, they show a doublet spectral pattern in Region III, similar to anorthite, but the two peaks in the doublet are 26-31 cm^{-1} apart, a wider split than those of anorthite, which are 15-20 cm^{-1} apart.

Conclusions: Based on Raman spectral patterns, multiplicity of peak groups, peak positions, and peak widths, seven types of feldspars with different chemical compositions and Al-Si ordering can be distinguished. Raman peak positions cannot, however, be used to determine small changes in Na^+/Ca^{2+} of plagioclases in a manner analogous to determining Mg^{2+}/Fe^{2+} of mafic silicates. In pyroxene and olivine, the distance between the Fe^{2+} or Mg^{2+} and the nearest O is ~2.1 – 2.2 Å[18], short enough that changing Mg^{2+}/Fe^{2+} affects the Si-O vibrational frequency continuously. In plagioclase, the distance between the Ca^{2+} or Na^+ and the nearest O is some 2.5 – 2.6 Å[18], too long for those cations to influence the Si – O vibrational frequency observably. An analogous situation holds for the alkali feldspars. The variation in the Na^+/Ca^{2+} in plagioclase is accompanied by a variation in Al(III)/Si(IV). Both the Al(III)/Si(IV) ratio and order-disorder in the tetrahedra may be responsible for the change in the Raman spectral features of plagioclase.

References: [1] Wang et al. (2002) *JGR,* accepted. [2] Wang et al. (2001) Am. Min.,*86*, 790-806. [3] Wang et al., (2001) *LPS XXXI, abstract #1887*. [4] Wang et al. (1995) JGR 100, 21,189-21,199. [5] P. H. Ribbe, *Feldspar Mineralogy,* 1983. [6] Zolai and Stout, *Mineralogy Concepts and Principles,* 1984. [7] von Manfried and von Stengel (1977) *Z. Krist.,146*,1-18.[8] Purcell and White, in *Microbeam Analysis – 1983*, R. Gookey, Ed., 289-292. [9] Sharma et al. (1983) *Am. Min.*, *68*, 11113-1125. [10] Velde and Boyer (1985) *Geophys.Res.*, *90*, 3675-3682. [11] Matson et al. (1986) *Am. Min., 71*, 694-704. [12] Salje (1986) *Phys.Chem.Min.*,13,140-346. [13] Velde et al. (1989) *Phys.Chem.Min,16*,436-441. [14] Heymann and Hörz (1990) *Phys.Chem.Miner.,17*,38-44. [15] Mernagh (1991) *J. Raman Spec.,22*,453-457. [16] Daniel et al. (1995) *Min.Mag.,59*, 25-33. [17] Daniel et al. (1997) *JGR*, 102,10,313-10,325. [18] Smyth & Bish, *Crystal structures & cation sites of the rock-forming minerals,(*1988) Allen & Unwin, Boston.

Table I. Raman Features of Feldspar minerals

Mineral Name	Chemical Composition	Structure & Ordering of Al-Si distribution	Characteristic Features of Strong Raman Bands		
			Region III [TO_4] modes	Region II [TO_4] & lattice modes	Region I lattice modes
Microcline	$KAlSi_3O_8$ (end member)	Triclinic, Highly ordered	513 476 453	285 265	157 126
Orthoclase	$KAlSi_3O_8$ (near end member)	Monoclinic, The Al and one Si disordered.	513-514 475 ± 2	282 ± 1	154 ± 2
Sanidine	$KAlSi_3O_8$ (near end member)	Monoclinic, The Al and all three Si disordered.	514 475 ± 1	284 ± 2	114 164 ± 2
Anorthoclase (K_Al-bite)	$Na_{\sim 0.6}K_{\sim 0.4}AlSi_3O_8$	Triclinic, Highly ordered	512.5 ± 0.5 474 ± 1	284	166
Low-T albite	$NaAlSi_3O_8$ (end members)	Triclinic, Highly ordered	507 479 456	290 ± 0.5	208 ± 1 184 ± 2 151
High-T Plagioclases	$Na_xCa_{1-x}Al_{1+x}Si_{3-x}$ (intermediate Na,Ca mixtures)	Triclinic, Structurally and compositionally disordered	509 ± 1 482 ± 2	284 ±3	179 ± 4
Anorthite & high Ca^{++}, low-T plagioclases	$CaAl_2Si_2O_8$ (end members)	Triclinic, Highly ordered	503 ± 1 484	285 250 ± 2	183 ± 2 140-150