A combined ToF-SIMS and EMP/SEM study of a three-phase symplectite in the Los Angeles basaltic shergottite

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Abstract–A rare three-phase symplectite consisting of Ca-rich pyroxene, Fe-rich olivine, and a silica phase is frequently found rimming pyroxene in the Martian meteorite Los Angeles. This assemblage is usually interpreted as the breakdown product of metastable pyroxferroite, a very rare pyroxenoid mineral itself. However, its origin is not entirely understood, mainly because the extremely small average size of the constituent phases represents a challenge for precise high-resolution analysis. In addition to electron microbeam methods, the present study uses time-of-flight secondary ion mass spectrometry (ToF-SIMS) to overcome the limits of spatial resolution and to comprehensively study this mineral assemblage. The prevailing breakdown hypothesis is supported by the following results: (1) The three symplectite phases are very homogenous in composition from 100 μ m down to the micrometer scale. (2) The silica phase could be shown to be almost pure SiO₂. (3) The symplectite bulk composition is consistent with pyroxferroite. Sub-micrometer sized Ti-oxide grains are found within the symplectite (but not within the Ca-rich pyroxene) and probably represent a minor breakdown phase in addition to the three main phases.

INTRODUCTION

The basaltic shergottite Los Angeles is one of the most differentiated Martian meteorites, i.e., it is rich in incompatible elements and late-state phases (Rubin et al. 2000). Its petrology is dominated by maskelynite and pyroxene. A three-phase symplectite is frequently found rimming Fe-rich pyroxene (Rubin et al. 2000). This symplectite consists of a fine intergrowth of Ca-rich pyroxene, Fe-rich olivine, and a silica-rich phase. Symplectites in general are not uncommon in terrestrial samples (e.g., Moseley 1984). The three-phase symplectite covered here, however, is only found in certain extraterrestrial samples.

Assemblages of this kind were first observed in lunar rocks (Ware and Lovering 1970) and interpreted as the breakdown products of metastable pyroxferroite, a rare pyroxenoid that had just been discovered in lunar rocks (Lunar Sample Preliminary Examination Team 1969; Lindsley and Burnham 1970). This interpretation was experimentally corroborated by Lindsley and Burnham (1970) and Lindsley et al. (1972). They demonstrated that such decomposition at low pressure (<<1 GPa) occurs when the pyroxferroite experiences temperatures of at least ~990 °C for more than three days (Lindsley et al. 1972). Pyroxferroite itself is a chain silicate (inosilicate) with the empirical formula (Ca_{~1/7}Fe_{~6/7})SiO₃ (Lindsley and Burnham 1970) that allows for Mg substitution at least up to $Mg_{\sim 1/7}$ (Lindsley et al. 1972). Therefore, its composition can be plotted in the quadrilateral of pyroxenes defined by its end members diopside, enstatite, ferrosilite, and hedenbergite (Fig. 1). However, pyroxferroite is not stable below ~1 GPa (Lindsley and Burnham 1970) and it does not crystallize in a pyroxene structure.

In addition to the lunar rocks returned by the Apollo missions, such three-phase symplectites were found in the



Fig. 1. Pyroxene quadrilateral for standard conditions (1000 hPa, 273.15 K). The zones for stable pyroxenes grow with increasing pressure and temperature. Also shown is the position of lunar pyroxferroite when cast into the pyroxene quadrilateral: it plots within the "forbidden zone" in which no stable phase with pyroxene crystal structure exists (Lindsley 1983).

lunar meteorites Elephant Moraine (EET) 96008 (Warren and Ulff-Møller 1999), Asuka-881757 (Oba and Kobayashi 2001) and likely launch-paired Miller Range (MIL) 05035 (Arai et al. 2007; Liu et al. 2007), Northwest Africa (NWA) 773 (Fagan et al. 2003), and Kalahari 009 (Sokol and Bischoff 2005). In almost all cases, the symplectites have been interpreted as a product of pyroxferroite breakdown. The only exception is NWA 773; here Fagan et al. (2003) explained the assemblage by formation directly from the melt during late stage crystallization because the silica-rich glass is not pure SiO₂ but contains up to 13 wt% of Al_2O_3 and up to 5 wt% of K_2O : these "feldspathic" components are not expected in a pyroxferroite precursor.

Similar three-phase symplectites consisting of Ca-rich pyroxene, Fe-rich olivine, and silica have been also found in the Martian meteorites Queen Alexandra Range (QUE) 94201 (McSween et al. 1996), Los Angeles (Rubin et al. 2000) and potentially launch-paired NWA 2800 (Bunch et al. 2008), as well as Shergotty (Aramovich et al. 2002). In these studies, Martian three-phase symplectites have been interpreted as breakdown products of metastable well. Aramovich et pyroxferroite as al. (2002)comprehensively explained how the late stage melt evolved to very Mg-poor compositions, eventually favoring crystallization of metastable pyroxferroite.

The authors also noted that the three-phase symplectite in Los Angeles is sometimes associated with a two-phase symplectite (Fe-rich olivine + silica) and a Ca-rich phosphate (merrillite). For these cases, they proposed an additional mechanism in which the simultaneous formation of merrillite during late-stage crystallization further lowers the local Ca and Mg concentration in the melt, favoring the formation of metastable pyroxferroite over unstable pyroxene.

Xirouchakis et al. (2002), however, reasoned that most Los Angeles symplectite was not formed by pyroxferroite breakdown, and they proposed an alternate 2-step mechanism. In their interpretation, unstable primary pyroxene exsolved to augite and pigeonite; then oxidepyroxene interaction, mainly between titanomagnetite and pigeonite, resulted in the observed complex assemblages. Some symplectite might also have been formed by direct decomposition of the primary pyroxene. Warren et al. (2004) rebutted this new interpretation in great detail, with the main arguments being that Xirouchakis et al. (2002) did not acknowledge the ubiquitous existence of the silica phase within the symplectites and that the modal abundance of Ca-rich pyroxene, Fe-rich olivine, and silica, when reconstructed into a single phase, is always consistent with a pyroxenoid precursor.

In their study of lunar meteorite MIL 05035, Liu et al. (2009) suggested that shock transformed primary pyroxferroite and pyroxene into three-phase symplectite and proposed this mechanism also for other lunar and Martian meteorites. Rubin et al. (2000) and Warren et al. (2004) argued against a shock related breakdown in case of Los Angeles because the symplectite contains shock induced faults. Moreover, since the breakdown conditions discovered by Lindsley et al. (1972) require temperatures greater than ~990 °C for more than three days and because shock events are very rapid on the order of seconds, Aramovich et al. (2002) precluded shock heating in general from being a viable mechanism for creating the symplectites. Yet Warren et al. (2004) discussed the possibility that the symplectites in Los Angeles did not assume their final detailed texture until after the last shock.

In summary, following mechanisms have been proposed or are conceivable to explain the three-phase symplectite in Los Angeles: (1) direct late stage crystallization of symplectite phases; (2) breakdown of metastable pyroxferroite that had been formed at low pressure (non-equilibrium); (3) breakdown of pyroxferroite that had been formed at high pressure (in equilibrium); (4) shock induced breakdown after (metastable) pyroxferroite; (5) oxide-pyroxene interaction after exsolution of primary metastable pyroxene into augite and pigeonit. Of these, (3) can almost certainly be ruled because Los Angeles demonstrably crystallized rather near the surface (Rubin et al. 2000; Xirouchakis et al. 2002) than in a depth of ~100 km, where a pressure of 1 GPa, necessary for pyroxferroite formation in equilibrium, would be reached on Mars. As pointed out above, (4) and (5) have been strongly rejected in previous studies (Rubin et al. 2000; Aramovich et al. 2002; Warren et al. 2004).

With this discourse in mind, our study addresses one basic difficulty in studying the symplectic mineral assemblages, which is that the small size of the intergrown phases represents a considerable analytical challenge. To measure mineral compositions, previous studies (e.g., Rubin et al. 2000; Xirouchakis et al. 2002; Aramovich et al. 2002; Warren et al. 2004) used electron microprobe (EMP) analysis, by recording the electron beam induced X-rays, in either wavelength dispersive (WDX) or energy dispersive (EDX) mode. However, the determined chemical compositions are inaccurate when the excited volume in the sample is larger than the smallest occurring phases. This is usually the case for the symplectites discussed herein. Therefore, the reported compositions were often those of the symplectite as a whole or were obtained from regions of exceptionally large individual phase patches—with the implicit assumption that these analyses are representative. Backscattered electron (BSE) images provide higher spatial resolution. However, since their contrast is proportional only to the mean atomic number and density, BSE images permit only discrimination of different phases, not accurate identification.

To overcome this predicament, we used time-of-flight secondary ion mass spectrometry (ToF-SIMS) in concert with electron microprobe based WDX and scanning EDX for element mapping. In recent years, ToF-SIMS has been successfully introduced in cosmochemistry as a valuable tool to determine elemental compositions (including minor and trace elements) with sub-micrometer spatial resolution (Stephan 2001). It has been applied to the study of interplanetary dust, presolar grains, CAIs in carbonaceous chondrites, and cometary samples from the Stardust mission. Previous studies of Martian meteorites using ToF-SIMS include the examination of exsolution lamellae in olivine from Chassigny (Greshake et al. 1998) and Nakhla (Greshake et al. 2000), polycyclic aromatic hydrocarbons (Stephan et al. 2003), and the formation of carbonates in Allan Hills (ALH) 84001 (Corrigan et al. 2003), as well as melt inclusions (Rost et al. 2001) and alteration products in Nakhla-type Martian meteorites (Rost et al. 2003; Rost and Vicenzi 2004; Rost et al. 2005; Vicenzi 2003).

The main benefit of applying ToF-SIMS is the ability to characterize the individual symplectite phases definitively, i.e., probing individual phase patches, even if <1 μ m, and examining the compositions of each component phases within the symplectite. Moreover, the concentration of many minor and trace elements (e.g., Li, Be, B, K, Ti, V, Cr, Mn, Co, Ni) can be determined for the individual phases, and accessory phases potentially overlooked in former studies can be recognized. Thus, this study should eventually provide further arguments to discriminate between the competing theories of symplectite formation.

ANALYTICAL METHODS

Quantitative mineral analyses were performed at the Museum für Naturkunde, Berlin, with a JEOL JXA-8800L electron microprobe operating at 15 kV and a beam current of 15 nA. The mineral standards used were certified by the US National Museum of Natural History (Smithsonian Institution) as reference samples for electron microprobe analysis (Jarosewich 2002). Bulk or "broad beam" WDX analyses of symplectite and adjacent pyroxene have been obtained by defocusing the electron beam to a diameter of ~10 μ m. X-ray elemental maps were acquired on the same electron microprobe at 15 kV accelerating voltage, 15 nA

beam current, and a beam size of 1 μ m. To detect the largest possible number of elements simultaneously, a Roentec EDR 288 EDX detector with an energy resolution of 139 eV was used for elemental mapping. The X-ray maps were acquired with a digital imaging system from 4pi Analysis Inc. During electron microprobe analysis, the excited sample volume strongly depends on the energy of the electrons and the atomic number of the elements present in the sample. Monte Carlo simulations using the CASINO 2 software (Drourin et al. 2007) show that for our analytical parameters the detected characteristic X-rays are typically generated at depths of 0.1–2.5 μ m. The lateral diameter of the excitation volume can easily reach 3 μ m. Carbon coating of the samples is required to prevent charging and thus maintain stable conditions.

ToF-SIMS measurements were carried out at Münster University with a TOF-SIMS IV instrument from ION-TOF GmbH. A detailed description of the instrument used in this study can be found in Stephan (2001). In brief, ToF-SIMS is a special SIMS variant in which a pulsed primary beam, in our instrumentation consisting of 69 Ga⁺ ions, is employed to sputter secondary particles from a sample surface. In contrast to the classic SIMS techniques based on mass separation by electric and magnetic fields, in ToF-SIMS all secondary ions of one polarity are measured quasi-parallel by recording their flight time to the detector.

Similar to other particle beam techniques, secondary ion distribution images can be obtained by scanning the focused primary ion beam over the sample area of interest. Since the interaction volume is on the nanometer-scale, the lateral resolution is limited by the spot size of the primary ion beam. For our instrumentation, the lateral resolution for insulating samples can be as small as ~0.3 μ m. Prior to the actual measurement, sample areas are sputter cleaned to remove omnipresent surface contamination and to amorphize the upper monolayers, i.e., making the analysis less susceptible to matrix effects (Stephan 2001).

Quasi-parallel ion detection and a high overall transmission up to 80% result in a high detection efficiency for all sputtered ions. This compensates for the rather low sputter rate, i.e., sample consumption, compared to classic SIMS: Only a few monolayers are removed during a typical ToF-SIMS measurement: 1–3 monolayers during sputter cleaning and typically <1 monolayer throughout the actual analysis. Also, by intermittently deploying electrons for charge compensation, coating of the sample with a conductive layer is not necessary. ToF-SIMS analyses, therefore, cause only minor alteration and destruction of sample material. Furthermore, the minimal thermal exposure of the sample compared to electron beam techniques enables the detection of volatile elements such as Na and K at high precision.

Quantitative results in SIMS are obtained by using element and material specific sensitivity factors derived from analogous standards. Since homogeneity on a micrometer scale is indispensable for ToF-SIMS standards, glass

100 μm Fig. 2. BSE image of the examined area in the Martian meteorite Los Angeles with the analyzed three phase symplectite in the center. Other phases are clinopyroxene (augite and pigeonite, cpx) ilmenite (il), ulvöspinel (us), maskelynite (mas). The upper left corner contains a close-up view of augite-pigeonite exsolution lamellae. Other frames indicate regions #1–3 of follow-up analyses shown in Fig. 3 (1) and Fig. 4 (2 and 3). The positions of EMP spot analyses

are given as a to e (cf. Table 1b).

standards are most appropriate. Although not quite analogous, they can be used to derive element concentrations in silicates that are correct to a factor of 1.1–1.5 (Stephan 2001). While this is less accurate for major elements than EMP analysis, ToF-SIMS is a valuable tool to determine the concentrations of minor and trace elements on a sub-micrometer scale.

RESULTS AND DISCUSSION

The three-phase symplectite examined in our study is shown in Fig. 2. As generally observed (Rubin et al. 2000), it is directly adjacent to pyroxene, which from now on will be also referred to as host pyroxene to avoid confusion with the Ca-rich pyroxene that is part of the symplectite. Warren et al. (2004) occasionally found a "transitional zone" between neighboring host pyroxene and the symplectite proper. Such a distinctive zone of highly predominant Ca-rich pyroxene with only minor Fe-rich olivine and silica is not seen in this instance of symplectite. The individual phases have dimensions of ~2–5 μ m (Ca-rich pyroxene and Fe-rich olivine) and ≤1 μ m (silica). The Ca-rich pyroxene constitutes a framework that is filled with olivine, within which the silica occurs as blebs. From this assemblage, several areas were selected for ToF-SIMS and EMP analyses at maximum lateral resolution (Fig. 2).

As outlined above, the measurements should help to discriminate between the main competing theories for symplectite formation, which are (1) breakdown after metastable pyroxferroite (or another metastable pyroxenoid) and (2) direct late stage crystallization. Assemblages resulting from these two mechanisms differ in the several points.

Si-rich phase. As one of the pyroxferroite breakdown phases, pure silica phase is to be expected, probably crystalline (tridymite). When formed during late stage crystallization, however, it would rather be a glass containing some Al_2O_3 as well. Moreover, it would serve as a major sink for alkali metals, i.e., contain a "feldspathic component."

Bulk composition. In the breakdown scenario, the overall and local composition of the symplectite would be indicative of the precursor phase, i.e., the composition should be that of a pyroxenoid and fall inside the "forbidden zone." On the other hand, late stage assemblages are not restricted to pyroxenoid compositions and should show varying local composition, reflecting the change in late stage melt composition during formation.

The breakdown material should also reflect the minor and trace element abundances of the former pyroxenoid. Although the partition coefficients for pyroxferroite are not known, most of them are probably comparable to those of pyroxene. Therefore, minor and trace element concentrations should be rather similar in the symplectite and the adjacent host pyroxene, reflecting only the evolution of the melt composition between pyroxene and pyroxenoid formation and the slightly different partition coefficients. Late stage assemblages, however, should be especially enriched in incompatible elements (e.g., K, P, Cl) and hence feature rather complementary minor and trace element signatures compared to the adjacent pyroxene.

Element Mapping

A typical $30 \times 30 \ \mu\text{m}^2$ close-up is shown in Fig. 3. It provides a direct comparison of the resolving power of SEM-BSE (Fig. 3a) and ToF-SIMS (Fig. 3b). Both images show the exsolution texture formed by the pyroxene as well as the fayalite and silica in-between. However, the ToF-SIMS image (Fig. 3b) reflects actual element concentrations. Figure 3c provides the masks or "regions of interest" used for quantitative ToF-SIMS analyses: For each phase, only the secondary ions coming from within the respective mask are evaluated. The compositions of the respective three phases are shown in Table 1 and will be discussed later. ToF-SIMSderived distributions of individual ion species are given in Fig. 3d. In addition to the phase forming major elements (Mg, Si, Ca, Fe), the distribution of the minor elements Na, Al, K, Ti, and Mn is displayed. Sodium and potassium are lowest within the silica phase, indicating the lack of a feldspathic





Fig. 3. BSE (a), ToF-SIMS (b and d), and EDX element images (e) from a $30 \times 30 \,\mu\text{m}^2$ region (#1 in Fig. 2). (b) ToF-SIMS three color overlay image: the intensities of the colors red, green, and blue are set proportional to the concentrations of Si, Ca, and Fe in such a way that the maximum concentration of each element corresponds to the highest respective color index. This image can be directly compared with the BSE image (a): the black/red areas represent silica (SiO₂), the dark gray/green regions Ca-rich pyroxene, and the light gray/blue areas Fe-rich olivine. The box in (b) marks the position of the profiles displayed in Fig. 5. (c) shows the "regions of interest" or masks selected for quantitative ToF-SIMS analyses (Table 1a and Fig. 7) superimposed on BSE image (a). To guarantee pure phase analyses, masks for the individual phases are restricted to the core regions, neglecting the transition domains. A series of ten ToF-SIMS secondary ion distribution images is given in (d). The number of counts/pixel is color coded and increases from black (zero) over blue, green, and yellow to red. The range of counts for the red pixels is given below each image. The streaks of high Na and K probably stem from contamination caught in little voids. EDX element mappings are shown in (e), with the same color coding as for the ToF-SIMS data.

Table 1a. Phase compositions for regions #1 and #2 (cf. Figs. 3 and 4) derived by ToF-SIMS. Given are element ratios relative to silicon^a.

	Ca-rich pyroxene			Fe-rich olivine			Silica		Bulk symplectite		Adjacent pyroxene	
	#1	#2	#2 ^b	#1	#2	#2 ^b	#1	#2	#1	#2	#1	#2
Li	$9.0(3) \times 10^{-5}$	$1.64(7) \times 10^{-4}$	$2.5(1) \times 10^{-4}$	$1.15(4) \times 10^{-4}$	$1.2(1) \times 10^{-4}$	$2.6(2) \times 10^{-4}$	$1.3(9) \times 10^{-6}$		$5.18(9) \times 10^{-5}$	$8.8(2) \times 10^{-5}$	$3.6(6) \times 10^{-5}$	$5.7(4) \times 10^{-5}$
Be	$4.0(5) \times 10^{-5}$	$2.7(8) \times 10^{-5}$	$2.4(9) \times 10^{-5}$						$1.0(1) \times 10^{-5}$	$1.2(2) \times 10^{-5}$		$8(4) \times 10^{-6}$
В	$2.0(2) \times 10^{-4}$	$7(4) \times 10^{-5}$	$1.8(4) \times 10^{-4}$	$1.7(2) \times 10^{-4}$	$5(3) \times 10^{-5}$	$1.2(7) \times 10^{-4}$	$8(3) \times 10^{-5}$		$1.38(6) \times 10^{-4}$	$1.0(1) \times 10^{-4}$	$3(2) \times 10^{-5}$	$5(2) \times 10^{-5}$
Na	0.01283(2)	0.01330(5)	0.01438(6)	0.00712(2)	0.00391(4)	0.00649(9)	$2.17(9) \times 10^{-4}$	$6.6(6) \times 10^{-4}$	0.005330(7)	0.00548(1)	0.00290(4)	0.00801(3)
Mg	0.0840(1)	0.1102(3)	0.1112(3)	0.1544(3)	0.1644(6)	0.221(1)	$7.6(3) \times 10^{-4}$	0.0113(4)	0.05762(6)	0.0779(1)	0.0974(4)	0.1058(3)
Al	0.02274(6)	0.0347(3)	0.0436(3)	0.00222(4)	0.0040(3)	0.0087(3)	0.00663(8)	0.0027(2)	0.00989(6)	0.0135(2)	0.0135(2)	0.0160(3)
Si	1.000(5)	1.000(5)	1.000(6)	1.000(6)	1.000(6)	1.000(7)	1.000(5)	1.00(1)	1.0000(4)	1.000(3)	1.000(4)	1.000(4)
Κ	$6.97(4) \times 10^{-4}$	$7.93(9) \times 10^{-4}$	0.00114(1)	$7.94(6) \times 10^{-4}$	$5.6(1) \times 10^{-4}$	0.00174(4)	$1.22(5) \times 10^{-4}$	$2.2(3) \times 10^{-4}$	$5.68(2) \times 10^{-4}$	$4.70(3) \times 10^{-4}$	$1.18(6) \times 10^{-4}$	$4.46(7) \times 10^{-4}$
Ca	0.2938(4)	0.3421(5)	0.3682(6)	0.02094(7)	0.0329(2)	0.0311(3)	0.00135(3)	0.0114(3)	0.08009(8)	0.1240(1)	0.1154(3)	0.1493(3)
Ti	0.0085(1)	0.0089(3)	0.0082(3)	0.00197(9)	0.0037(3)	0.0020(4)	$8.2(1) \times 10^{-4}$	$9(2) \times 10^{-4}$	0.00435(6)	0.00378(9)	0.0062(4)	0.0062(2)
V	$1.56(6) \times 10^{-4}$	$3.0(1) \times 10^{-4}$	$2.0(2) \times 10^{-4}$	$1.7(2) \times 10^{-5}$	$7(1) \times 10^{-5}$		$3(2) \times 10^{-6}$		$4.0(2) \times 10^{-5}$	$9.3(4) \times 10^{-5}$	$1.4(2) \times 10^{-4}$	$1.6(1) \times 10^{-4}$
Cr	$1.0(2) \times 10^{-5}$	$2.4(5) \times 10^{-5}$	$2.2(6) \times 10^{-5}$	$2(1) \times 10^{-6}$					$3.9(5) \times 10^{-6}$	$9(1) \times 10^{-6}$	$0.8(5) \times 10^{-6}$	$2.0(5) \times 10^{-5}$
Mn	0.0103(3)	0.0144(7)	0.0143(7)	0.048(1)	0.049(3)	0.067(4)	$8(1) \times 10^{-5}$	0.0029(3)	0.0137(3)	0.0172(6)	0.0191(5)	0.0203(7)
Fe	0.559(3)	0.571(3)	0.579(4)	2.633(4)	2.112(5)	2.845(8)	0.0062(2)	0.109(2)	0.745(1)	0.710(2)	0.644(2)	0.823(2)
Co	$8(4) \times 10^{-5}$		$4(1) \times 10^{-5}$	$4(2) \times 10^{-4}$		$8(5) \times 10^{-4}$			$1.13(6) \times 10^{-4}$	$1.3(1) \times 10^{-4}$		$1.6(2) \times 10^{-4}$
Ni	$2(1) \times 10^{-5}$	$1.0(6) \times 10^{-4}$		$5(3) \times 10^{-5}$								

^aRatios of atomic abundances obtained by application of element specific sensitivity factors (Stephan 2001); errors are 1*σ*, given as last significant digit in parentheses. ^bLarge areas that were selected separately in Fig. 4d.

	Ca-ric	h pyroxene		Fe-rich olivine	Bulk	Adjacent	
	#a	#b	#c	#d	#e	symplectite ^b	pyroxene
0	2.98	3.05	3.90	3.62	3.94	3.01	3.04
Na	0.0036	0.0073	0.0012		0.0015	0.0043	0.0035
Mg	0.0939	0.108	0.147	0.108	0.119	0.0799	0.120
Al	0.016	0.019	$4.7 imes 10^{-4}$	0.0021		0.015	0.016
Si	1.00	1.00	1.00	1.00	1.00	1.00	1.00
K		$1.3 imes 10^{-4}$	3.7×10^{-4}		4.4×10^{-4}	$5.4 imes 10^{-4}$	
Ca	0.209	0.365	0.012	0.035	0.0080	0.166	0.210
Ti		0.010	0.0049	0.0068	0.0029	0.0068	$1.8 imes 10^{-4}$
Cr		$7.5 imes 10^{-4}$	$6.5 imes 10^{-5}$	$1.1 imes 10^{-4}$	$1.8 imes 10^{-4}$	$1.7 imes 10^{-4}$	$1.8 imes 10^{-4}$
Mn	0.012	0.014	0.036	0.034	0.034	0.016	0.017
Fe	0.639	0.507	1.70	1.42	1.77	0.684	0.665
Ni	$7.8 imes10^{-4}$	2.4×10^{-4}		0.0029		$4.9 imes 10^{-4}$	

Table 1b. Phase compositions derived by EMP/WDX analysis (cf. Fig. 2). Given are element ratios normalized to silicon^a.

^aAfter ZAF matrix correction; errors estimated 0.1% for major elements, at least 1% for minor elements.

^bGeometric mean of 11 measurements, "not detected" concentrations omitted.

component. This finding is in accordance with the breakdown hypothesis.

The distribution of Mn corresponds with that of Fe, as Mn^{2+} ions often occupy the same crystal positions as Fe^{2+} and Mg^{2+} ions in silicates. Na, Al, and Ti basically show the same distribution as Ca, i.e., having the highest concentration within the pyroxene. This is expected since the crystal structure of olivine (fayalite) is rather inflexible and disfavors the incorporation of these elements. On the other hand, the clinopyroxene crystal structure allows their integration more readily.

In addition to its occurrence in the pyroxene, some Na appears in streaks where also most of the K is found. The streaks show no correlation with any of the major symplectite phases but are correlated with C_2^- and appear where Si, Ca, and Fe are low (cf. black streaks in Fig. 3b). These findings indicate that some surface contamination got trapped in small voids or fractures, probably during the polishing procedure.

Apart from occurring in pyroxene, Ti is highly concentrated in several $\leq 1 \ \mu m$ sized spots. These locations appear almost black in the Si-Ca-Fe overlay image (Fig. 3b); however, the Fe intensities are slightly higher in these spots compared to the surrounding silica. These spots probably represent Fe bearing Ti oxides, e.g., rutile or ilmenite, that seem to be a rare component of the symplectite in general: While Xirouchakis et al. (2002) found "tiny bits of Fe-Ti oxides" in the symplectite, their spatial resolution was not sufficient to detect the sub-micrometer sized Ti oxide identified in this study.

The ToF-SIMS secondary ion distribution images (Fig. 3d) are juxtaposed with those obtained by electron microbeam mapping of the very same area (Fig. 3e). These EDX images suffer from a reduced dynamic range of intensities. It is only in the larger phase patches that the Fe and Ca signal reflects the actual enrichment in the respective phases. The expected correlations of Mg and Al with Ca, and of Mn with Fe are barely noticeable. Phase boundaries are poorly defined. Concerning Ti, only some Ti-oxide spots are discernible but not the enrichment in pyroxene that was observed with ToF-SIMS. The reason for these limitations is the large excitation volume for X-rays, which exceeds the size of the smallest phase patches analyzed. Therefore, precise electron microbeam based characterization of the symplectite is possible only for a few exceptionally large phase patches.

We like to note that we chose EDX mapping because it provided the full spectrometric information in a single run whereas our available WDX instrumentation would have provided only four elements per run. Multiple runs, however, bear the risk of damaging the sample or inflicting charging. Shifted or distorted imagery would have complicated a comparison with ToF-SIMS mappings. WDX mappings often seem to look superior to EDX mappings because the energy resolution is better and peak intensities are higher, resulting in a better signal to noise ratio for individual peaks, i.e., high contrast. The spatial resolution, however, depends not on the method of X-ray detection and is the same for WDX and EDX.

Two other close-ups of the symplectite allow identification of additional accessory phases (Fig. 4). The region #2 (Figs. 4a-d) contains one ~3 µm large Al,Si,K-rich and Mg,Fe-poor phase, probably feldspar or maskelynite. Another $\sim 1 \,\mu m$ sized phase is characterized by high intensities of Ca⁺, Cl⁻, and PO₂⁻, suggesting chlorapatite. In region #3 (Fig. 4e), at least two different accessory phases can be recognized. As previously seen in Fig. 3, some ~1 µm sized Ti-rich phases, probably Ti oxides, occur enclosed by olivine and silica, but not within the Carich pyroxene. Several ~1 µm sized S-bearing phases indicate sulfide or sulfate, located again only outside pyroxene. Similar sulfur-rich phases were also observed by Xirouchakis et al. (2002) who reported "tiny bits of [...] pyrrhotite." An Al,K-rich phase on the left is ~10 µm in size and has a similar composition than the maskelynite adjacent to the right of the symplectite (cf. Fig. 2). Both phases might have been connected in the third dimension before thin section preparation, as was assumed for a similar observation by Warren et al. (2004). The ~1 µm sized K streaks in Fig. 4e are most likely caused by contamination in sample fractures or symplectite voids as seen in region #1 (Fig. 3d).

Profiles

Intensity profiles derived from ToF-SIMS and EDX analyses of the same location (cf. Fig. 3b) are shown in Fig. 5. The phases, from left to right, are Ca-rich pyroxene, silica, Ca-rich pyroxene, silica, Fe-rich olivine, silica, Ca-rich pyroxene, silica, and Fe-rich olivine. Element intensities are given for Na, Mg, Al, Si, K, Ca, Ti, Mn, and Fe.

The X-ray scans show considerably less variation in intensity than those obtained from ToF-SIMS analysis. Only the Ca profile allows discrimination of the phases, but the resolution is significantly lower than in the ToF-SIMS data. In case of Fe, X-ray mapping shows the correct trend for the right part of the profile, except for the Fe-free silica that could not be resolved. In the left part of the profile, however, an intensity peak indicates olivine where actually a silica phase enclosed by pyroxenes is exposed at the sample surface (cf. Si, Ca, and Fe ToF-SIMS profiles). Here, the EDX signal likely has a significant contribution from an Fe-rich olivine underneath the exposed minerals. Likewise, EDX profiles of the other elements are not correlated with the exposed phases from the symplectite. For instance, the only peak in the EDX scan of Ti is probably caused by a deeper lying Ti-oxide phase as well. This substantiates the inference that electron microbeam based techniques are unable to analyze the Martian three-phase symplectite in detail.

In contrast, the ToF-SIMS profiles provide qualitative



Fig. 4. Accessory phases found in regions #2 and #3 (Fig. 2). Secondary ion distribution images (a), BSE image (b), and ToF-SIMS three color overlay image (c) are from a symplectite "finger" surrounded by pyroxene. Alkali feldspar becomes apparent in 27 Al⁺ and 39 K⁺ distribution images. The spots in 35 Cl⁻ and PO₂⁻ (correlated with 40 Ca⁺) are probably indicative of chlorapatite. Composite image (d) shows the "regions of interest" or masks selected for quantitative ToF-SIMS analyses (Table 1a and Fig. 7), overlain on top of the BSE image (a). The symplectite shown in (e) features at least two accessory phases: Ti-rich grains (probably oxides) and S-rich spots (probably sulfides). The Al-rich phase on the left is probably maskelynite, which is the neighboring phase to the right. K-enrichment in tiny voids or fractures indicates contamination.

information about the element concentrations in individual phases without interference from adjacent phases. This allows the documentation of several chemical trends in the threephase assemblage. Magnesium has roughly the same abundance in olivine and pyroxene. Aluminum occurs in pyroxene and silica but not in olivine. Titanium is correlated with Ca and consequently enriched in pyroxene, whereas Mn strongly correlates with Fe and is mainly found in olivine and in lower concentrations in pyroxene. Of all symplectite phases, the silica phase has the lowest concentrations of Na, Mg, K, Ca, Ti, Mn, and Fe. This is contradictory to the mechanism of direct late stage crystallization in which the forming glass would accommodate most of the remaining Na and K.

The discussion of chemical trends will be continued in the following section. Note that Na and K are most enriched in a sample fracture, a contamination incurred during sample preparation. Lateral resolutions of 1.5 μ m for EDX analysis and 0.35 μ m for ToF-SIMS analysis were inferred from the steepness of the profile at phase boundaries, i.e., the distance in which the intensity changes by $(1-1/e) \approx 63\%$, symmetrically measured around the boundary location. Only the resolving power of ToF-SIMS is sufficient to analyze all three phases of the symplectite individually.

Composition

The BSE images Fig. 2 and Fig. 4b show that the host pyroxene represents not a single phase but is exsolved into ~200 nm thin lamellae, usually being augite and pigeonite. Therefore, the bulk compositions of the host pyroxene and the symplectite were approximated by defocused beam electron microprobe analysis and by large area quantitative ToF-SIMS analysis. ToF-SIMS results, normalized to Si, are given in



Fig. 5. Intensity profiles across several patches of the three-phase symplectite as derived by the ToF-SIMS (black lines) and EDX (gray lines) measurements presented in Fig. 3. To improve counting statistics, raw intensities have been added for a 0.4 μ m stretch perpendicular to the profile direction. Each individual element profile is plotted normalized to the maximum (maximum intensity = 100). The location of these profiles is given in Fig. 3b; the respective strip from the BSE image is shown at the top of the figure, together with the labels indicating the phases exposed at the surface of the thin section, i.e., px: Ca-rich pyroxene, ol: Fe-rich olivine, si: silica, and f: fracture containing Na and K contamination.

Table 1a, including individual compositions of the constituent phases of regions #1 and #2 (cf. Fig. 2). The tabulated abundances are all relative to Si and by atom numbers. They have been corrected by using the element specific sensitivity factors for silicates as published in Stephan et al. (2001).

Symplectite phases, bulk symplectite and adjacent pyroxene are plotted together in the pyroxene quadrilateral in Fig. 6. The results are in good agreement with previous studies of symplectites in lunar rocks and Martian meteorites (Lindsley and Burnham 1970; Lindsley et al. 1972; Aramovich et al. 2002). The symplectite compositions fall within the "forbidden zone" and are hence consistent with the hypothesis of a metastable pyroxenoid precursor. Moreover, their composition lies in the field of lunar pyroxferroite. The overall composition of the adjacent host pyroxene is very similar to that of the symplectite. Fe/Mg-ratios are higher in



Fig. 6. Compositions of bulk symplectite, its olivine and pyroxene phases, and adjacent host pyroxene (data taken from Table 1a). For comparison, symplectite and olivine are plotted together with the pyroxenes based on their Mg,Fe,Ca-composition. 0.5 GPa and 1 GPa boundaries of the "forbidden zone" were taken from Lindsley (1983). Filled symbols indicate measurements from symplectite region #1, open symbols are from symplectite region #2 (cf. Fig. 2).

the symplectite compared to the adjacent pyroxene. This observation is consistent with an evolution of the residual melt during late stage crystallization as suggested by Aramovich et al. (2002); as the melt is getting increasingly depleted in Mg the composition of the forming pyroxenoid moves further into the "forbidden zone," eventually reaching the field of pyroxferroite. It is interesting to note that the symplectite composition of the "finger" region #2 has a slightly lower Fe/Mg-ratio than symplectite region #1, bringing it very close to the composition of the adjacent pyroxene, which in this case is only micrometers away, enveloping region #2. On the other hand, the Fe-richer symplectite in region #1 is further away from the pyroxene, already adjacent to ilmenite. Although the host pyroxene compositions fall within the "forbidden zone," the pyroxene is not metastable anymore since it already exsolved into augite and pigeonite.

The "forbidden zone" of inhibited pyroxene formation at 0.5 GPa and 1 GPa (Lindsley 1983) is indicated in Fig. 6. Stable or equilibrium formation of a symplectite precursor would have required a pressure >0.8 GPa, corresponding to a depth >70 km below the Martian surface. As pointed out before, this is not a viable process since a shallow formation of Los Angeles is generally accepted (Rubin et al. 2000; Xirouchakis et al. 2002).

The ToF-SIMS derived element concentrations from Table 1a are plotted in Fig. 7 normalized to Si and the mean element contents of the host pyroxene. This helps to show how the symplectite (and hence the potential former pyroxferroite) composition differs from the earlier formed pyroxene, and also how the minor and trace elements of the pyroxferroite have been redistributed among the constituent phases of the symplectite.

The data sets from the two symplectite regions #1 and #2 plot closely together. The only major difference is in silica. Since the phases in region #2 are significantly smaller than in region #1, even ToF-SIMS is at its limit concerning lateral resolution. Therefore, the element concentrations in silica of region #2 should be considered as upper limits.

Not only the previously discussed Mg, Fe, and Ca concentrations (position in the quadrilateral, Fig. 6) of bulk symplectite and host pyroxene are very similar but basically all analyzed elements with the possible exception of Ti. Subtle chemical trends are discernible though. Magnesium, Al, Ca, Ti, and Mn concentrations are slightly lower in the symplectite, while K and maybe Li tend to be enriched in the symplectite relative to the adjacent host pyroxene. Sodium and iron show no differences between pyroxene and symplectite. Titanium is obviously depleted (~35%) in the symplectite relative to the adjacent host pyroxene. With the bulk symplectite representing the pyroxferroite composition, these trends may either indicate an evolution of melt composition or document slightly different partition coefficients for pyroxferroite and the metastable pyroxene or pyroxenoid that later decomposed into the augite and pigeonite pyroxene. The Ti depletion in the symplectite could be a consequence of beginning parallel crystallization of Ti-oxides like ilmenite and ulvöspinel.

Since there are only minor differences in composition between symplectite and adjacent host pyroxene, which can easily be explained by the evolving melt and/or different partition coefficients, the data is fully consistent with the idea that a precursor material of the symplectite crystallized next in sequence to the pyroxene. As discussed earlier, the symplectite composition itself supports the hypothesis that this precursor material was pyroxferroite. As for the idea of potential direct late stage crystallization, it seems unlikely that a mix of three late stage minerals adds up to a composition so close to the previously formed pyroxene.

For the element concentrations within the individual symplectite phases, Fe-rich olivine has higher contents of Mg, Mn, and Fe, whereas the Ca-rich pyroxene has higher contents of Na, Al, Ca, and Ti. The latter trend also applies to Be, V, and Cr (Table 1) although these elements could not be detected in all phases and are therefore not plotted in Fig. 7. All shown element concentrations are very low in the silica phase, consistent with almost pure SiO₂. This partitioning of element contents amongst the three symplectite phases is also consistent with a pyroxferroite precursor material in the sense that pure silica, probably crystalline, could form while the minor and trace element budget is accommodated by the olivine and pyroxene. As



Fig. 7. Si-normalized element abundances of the studied phases relative to the average composition of the adjacent host pyroxene (data taken from Table 1a). Filled symbols indicate measurements from symplectite region #1, open symbols are from symplectite region #2 (cf. Fig. 2). Compositions of host pyroxene were obtained from measurements taken close to the respective symplectite regions. Pyroxferroite, the supposed precursor material of the three-phase symplectite, would have the composition of bulk symplectite. Statistic errors are smaller than symbols.

pointed out before, in a late stage, direct crystallization scenario, especially the alkali metal elements would rather end up in a silica-rich "feldspathic" glass.

Quantitative EMP/WDX results are given in Table 1b, which provides the compositions of two larger patches of Ca-rich pyroxene and of three larger patches of Fe-rich olivine from the symplectite, as well as the compositions of bulk symplectite and adjacent host pyroxene, derived by broad beam analysis. In general, the compositions of individual phases do not compare very well with the ToF-SIMS data. The EMP data suffer from multiple phases mixing in the measurements due to the limited spatial resolution of the applied method. For example, the composition of Fe-rich olivine #d appears too low in O and Fe, and too high in Ca. The effect of mixed phase analyses is especially crucial for minor elements (Ti, Cr, Mn, Ni) that often show substantial variation with regard to the individual symplectite phases. The broad beam analyses of bulk symplectite and pyroxene, however, are in excellent agreement with the respective ToF-SIMS results (Table 1a), as the quality of the obtained data is not limited by the lateral resolution of the applied methods.

Since previous studies faced the problem of insufficient spatial resolution, compositions of the individual symplectite phases had to be derived from rather large phase patches (>1-2 μ m) that might not be representative of the average composition of the respective phase. The ToF-SIMS measurements of this study, however, offer a means to validate this approach. Table 1a provides the relative element concentrations in two larger phase patches from

symplectite region #2 (Fig. 4d). The individual composition of the Ca-rich pyroxene matches the average composition of the phase in this region extremely well; differences are all of the same order as variations between fine grained Ca-rich pyroxenes in #1 and #2. The same holds when comparing the larger, individual Fe-rich olivine patch with the fine grained Fe-rich olivines of region #1 and #2; only Li and Al deviate by a factor of about two. These findings indicate that, indeed, it seems to be a valid approach to use the compositions of some larger patches as a proxy for the difficult to measure concentrations in the sub-micrometer sized structures.

SUMMARY AND CONCLUSIONS

This study employed ToF-SIMS to complement electron microbeam analyses of the three-phase symplectite found in the Los Angeles Martian meteorite. The high spatial resolution and the ability to simultaneously measure a wide range of elements down to trace levels proved to be key in achieving a higher level of understanding of the symplectite and its formation. A welcome bonus is the negligibly small sample consumption, only 1–4 monolayers. This makes ToF-SIMS highly suitable for the analysis of any small (and precious) samples like, e.g., IDPs, presolar grains, and cometary samples.

The three main phases of the symplectite, i.e., Ca-rich pyroxene, Fe-rich olivine, and silica, were analyzed individually with sub-micrometer resolution. The results corroborate the prevailing interpretation of the three-phase symplectite as a breakdown product of pyroxferroite. The pyroxferroite itself crystallized just after the neighboring pyroxene during rapid cooling, when the melt composition became too Fe-rich to form genuine pyroxene. Previous electron microbeam studies could only analyze the bulk symplectite and the few exceptionally large patches of pyroxene and favalite: they could not resolve the often <0.5 um sized silica phase. The ToF-SIMS results now demonstrate the essentially uniform composition of the Ca-rich pyroxene and Fe-rich olivine down to the sub-micrometer scale. Furthermore, they demonstrate that the third phase, commonly deduced to be silica, is indeed almost pure SiO₂. This indicates crystalline silica rather than glass, possibly tridymite. Tridymite is the stable quartz polymorph at low pressure and temperatures necessary for pyroxferroite breakdown (>990 °C). Therefore, it was assumed to be the silica phase emerging from this process early on (Lindsley and Burnham 1970: Lindslev et al. 1972). ToF-SIMS and EMP results show the expected trend of Fe enrichment during pyroxene/pyroxferroite crystallization. Furthermore, several minor and trace element concentrations were determined for all breakdown phases, all consonant with the expected partitioning between the phases.

The observed sub-micrometer sized Ti oxides (and probably the S-rich phases too) occur only amongst the Ferich olivine and silica and are not associated with the Ca-rich pyroxene. This textural setting suggests that the TiO₂ pyroxferroite the primary was contained in first the Ca-rich pyroxene accommodated bv during decomposition. Once the primary silicates and especially the Ca-rich pyroxene were saturated with TiO₂, separate Ti oxides formed.

In summary, the observations outlined above indicate a single-stage process for the pyroxferroite breakdown: The pyroxferroite decomposed directly into Ca-rich pyroxene, Ferich olivine, silica, less abundant Ti oxides and potentially other scarce and minute phases containing those elements that disfavor incorporation into olivine and the probably crystalline silica.

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