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^{39}Ar–^{40}Ar ages of martian nakhlites

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Abstract

We report ^{39}Ar–^{40}Ar ages of whole rock (WR) and plagioclase and pyroxene mineral separates of nakhlites MIL 03346 and Y-000593, and of WR samples of nakhlites NWA 998 and Nakhla. All age spectra are complex and indicate variable degrees of ^{39}Ar recoil and variable amounts of trapped ^{40}Ar in the samples. Thus, we examine possible Ar–Ar ages in several ways. From consideration of both limited plateau ages and isochron ages, we prefer Ar–Ar ages of NWA 998 = 1334 ± 11 Ma, MIL 03346 = 1368 ± 83 Ma (mesostasis) and 1334 ± 54 Ma (pyroxene), Y-000593 = 1367 ± 7 Ma, and Nakhla = 1357 ± 11 Ma, (2σ errors). For NWA 998 and MIL 03346 the Ar–Ar ages are within uncertainties of preliminary Rb–Sr isochron ages reported in the literature. These Ar–Ar ages for Y-000593 and Nakhla are several Ma older than Sm–Nd ages reported in the literature. We conclude that the major factor in producing Ar–Ar ages slightly too old is the presence of small amounts of trapped martian or terrestrial ^{40}Ar on weathered grain surfaces that was degassed along with the first several percent of ^{39}Ar. A total K–^{40}Ar isochron for WR and mineral data from five nakhlites analyzed by us, plus Lafayette data in the literature, gives an isochron age of 1325 ± 18 Ma (2σ). We emphasize the precision of this isochron over the value of the isochron age. Our Ar–Ar data are consistent with a common formation age for nakhlites. The cosmic-ray exposure (CRE) age for NWA 998 of ~12 Ma is also similar to CRE ages for other nakhlites.
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1. INTRODUCTION

Nakhlites are the second most abundant group of martian meteorites and currently consist of Nakhla, Lafayette, Governador Valadares, NWA (Northwest Africa) 817, NWA 998, the paired group Y (Yamato) 000593/749/802, and MIL (Miller Range) 03346 (Meyer, 2004). Nakhlites are thought to be cumulates that formed subsurface (Reid and Bunch, 1975; Berkley et al., 1980; Harvey and McSween, 1992; McSween, 1994), and they appear to have cooled relatively slowly under oxidizing conditions (Mikouchi and Miyamoto, 1998, 2002). Nakhlites experienced lower shock levels than any other martian meteorites, and their plagioclases have not been converted to maskelynite (Fritz et al., 2005). A detailed review of nakhlites was presented by Treiman (2005). Additional description of nakhlites studied is given in Electronic annex EA-1.

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Unlike martian shergottites, whose formation ages appear to vary considerably (Nyquist et al., 2001; Gaffney et al., 2007; Bouvier et al., 2008), the nakhlites appear to have very similar, if not identical radiometric ages of ~1.3 Ga. Nyquist et al. (2001) summarized for Nakhla, Lafayette, and Governador Valadares radiometric ages measured by various techniques, which span the range 1.19 ± 0.02 Ga to 1.37 ± 0.02 Ga. These authors gave "preferred" ages of Nakhla = 1.27 ± 0.01 Ga, Lafayette = 1.32 ± 0.02 Ga, and Governador Valadares = 1.33 ± 0.01 Ga. Since this review, other radiometric ages have been reported. For Y-000593, Misawa et al. (2005) reported ages of Rb–Sr = 1.30±0.02 Ga and Sm–Nd = 1.31 ± 0.03 Ga, and Nakamura et al. (2002) reported a Rb–Sr isochron age of 1.269 ± 0.240 Ga. Shih et al. (2006) reported a Rb–Sr isochron age of 1.29 ± 0.12 Ga and a Sm–Nd isochron age of 1.36 ± 0.03 Ga for MIL 03346. Carlson and Irving (2004) reported a preliminary Sm–Nd age for NWA 998 of 1.29 ± 0.05 Ga. More recently, Swindle and Olson (2004) reported whole rock Ar–Ar ages, based on partial plateaus, of 1.322 ± 0.010 Ga for Lafayette and 1.323 ± 0.011 Ga for Nakhla. Some preliminary Ar–Ar ages for nakhlites have been reported by Anand et al. (2006) and Shankar et al. (2008). In addition, the Chassigny dunite gives Ar–Ar, Rb–Sr, and Sm–Nd ages very similar to the nakhlites (Nyquist et al., 2001).

Although most radiometric ages of nakhlites strongly suggest a common formation time about 1.3 Ga ago, the reason for the total variation in individual ages over about 0.2 Ga is not obvious. The small errors on some of these ages might suggest real differences in formation times among these nakhlites. Further, ^{39}Ar–^{40}Ar ages for some nakhlite analyses gave complex releases that may have been influenced by martian weathering, ^{39}Ar recoil effects, or the presence of a trapped ^{40}Ar component not produced by *in situ* decay of K. To address these issues, in this paper we present eight new Ar–Ar ages of whole rock and/or mineral separates of four nakhlites, NWA 998, MIL 03346, Y-000593, and Nakhla. The first three nakhlites in this list were found relatively recently, and ages for the first two have only been reported in abstract form. These new Ar–Ar data show complex age spectra. Consequently, we examine the data in great detail in multiple ways in order to ascertain both the reason for such complexity and the preferred Ar–Ar age. Because Ar–Ar ages have now been reported for six nakhlites, we also examine all these data in a total K versus ^{40}Ar isochron plot to determine the degree of concordance of Ar–Ar ages of nakhlites.

2. SAMPLES AND EXPERIMENTAL METHODS

We received from A. Irving a plagioclase-enriched (Plag) sample of NWA 998 initially produced by flotation in bromoform (Carlson and Irving, 2004). At JSC this sample was sieved into grain-size fractions, and a sample of the 74-149 micron fraction was taken for Ar–Ar analysis. The relatively pure, mineral-separated olivine of NWA 998 used to measure cosmogenic noble gases also was provided by A. Irving. We analyzed WR samples of MIL 03346 and Y-000593 that were allocated to JSC. Later we obtained separate samples of these two nakhlites that were allocated to K. Nagao. These samples were gently crushed in a boron carbide mortar and divided into grain sizes of 100–200 mesh (149–74 μm) at JSC by J. Park and C.-Y Shih. Plagioclase and mesostasis were concentrated using heavy liquids with a density cut at <3.32 g/cm^3, using methylene iodide. For pyroxene separates, we used thallium malonateformate (Clerici's solution) to collect density fractions of $3.32 < \rho < 3.70$ g/cm^3. The separated pyroxene samples for nakhlites appear greenish in color. The feldspathic sample of MIL 03346 is mostly mesostasis, for which most K probably resides in fine-grained, vitrophyric, intercumulus opaque glasses comprising ~26% of the mesostasis (Treiman, 2005; Day et al., 2006; Imae and Ikeda, 2007). Because there is no (or very little) plagioclase in our feldspathic separate of MIL 03346, we call it Meso. Portions of these mineral separates for MIL 03346 were sent to K. Nagao (University of Tokyo) for further noble gas analyses. We analyzed a WR sample of Nakhla. Relevant nakhlite characteristics of relative cooling rates, weathering, and grain size for K-containing minerals are discussed in EA-1 and must all be considered in interpreting Ar–Ar age data.

The eight nakhlite samples discussed above were neutron irradiated at the University of Missouri reactor for 120 h in multiple irradiations spread over 5 years. The irradiation parameters (*J*-values) were determined from 7 to 10 samples of the NL-25 hornblende included with each irradiation. The irradiation year and determined *J*-value for each analyzed sample were: NWA 998, 2004, $J = 0.02077 \pm 0.00009$; Y-000593 WR, 2003, $J = 0.02565 \pm 0.00012$; MIL 03346 WR, 2005, $J = 0.02110 \pm 0.00008$; MIL 03346 Meso and Y-000593 Plag, 2006, $J = 0.02315 \pm 0.00010$; MIL 03346 Pyx and Y-000593 Pyx, 2007, $J = 0.02335 \pm 0.00012$ and 0.02355 ± 0.00008, respectively. A whole rock sample of Nakhla was irradiated in 2002 and gave a *J*-value of 0.02565 ± 0.00013. Each nakhlite sample was degassed of its Ar by stepwise heating (typically for 20 min) in a deep well, Ta crucible outfitted with a thermocouple and heated by induction. The Ar released was purified on metal getters and its isotopic composition was measured on a VG-3600 mass spectrometer. Corrections were applied for instrument mass discrimination, extraction blanks, and isotopic interferences produced in the reactor. Ages were calculated relative to the age of the Nl-25 hornblende (2.65 Ga) using the K decay parameters reported by Steiger and Jäger (1977). Characteristics of the NL-25 hornblende standard and experimental details are given in Bogard et al. (1995, 2000). Nakhlite Ar–Ar data are reported in *Electronic* annex EA-2.

3. AGE SPECTRA RESULTS

3.1. NWA 998 Ar–Ar

The Ar–Ar age spectrum for the plagioclase separate of NWA 998 is shown in Fig. 1. High K/Ca and ^{36}Ar/^{37}Ar ratios and low ages in the first few extractions suggest grain surface weathering, typical of hot desert meteorites, and

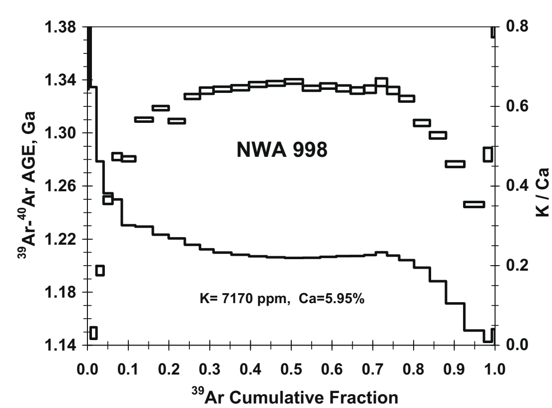

Fig. 1. ^{39}Ar–^{40}Ar ages (rectangles, left *Y*-axis) and K/Ca ratios (stepped line, right *Y*-axis) for stepwise temperature release of a plagioclase-enriched sample of nakhlite NWA 998. K and Ca concentrations are indicated.

we do not further consider these data. Ages and K/Ca ratios are relatively constant for ^{39}Ar releases over 24–81%. These represent plagioclase, and show similar K/Ca ratios to those plagioclase data reported by Treiman (2005) and Treiman and Irving (2008). For >81% total ^{39}Ar release, a decrease in the K/Ca reflects Ar degassing from pyroxene contaminants in the Plag separate, which was not pure. A correlated decrease in the age probably reflects the recoil of ^{39}Ar during its production in the reactor, out of phases rich in K and releasing at low temperature, and into this pyroxene phase. Such ^{39}Ar recoil is commonly observed in ^{39}Ar–^{40}Ar dating when relatively K-rich and K-poor grains are irradiated in contact (Huneke and Smith, 1976). Addition of ^{39}Ar to the pyroxene depresses the ^{40}Ar/^{39}Ar ratio and the age at higher temperatures. Thus, to derive an Ar–Ar age for NWA 998 from Fig. 1, we consider only that Ar data at intermediate temperature release, which probably was not affected by ^{39}Ar recoil. The average age for 15 extractions releasing 24–81% of the ^{39}Ar is 1334 ± 11 Ma (2σ). The age uncertainty reflects uncertainties in measuring and correcting Ar isotopic ratios and the uncertainty in the irradiation constant (J), but not systematic uncertainties in the absolute age of the NL-25 age monitor or in the ^{40}K decay parameters (Bogard et al., 2000). For purposes of comparing relative Ar–Ar ages obtained at JSC, these latter two uncertainties do not apply.

We examine the NWA 998 data in isochron plots to assess whether or not trapped ^{40}Ar in NWA 998 artificially increases the age we quote above. (See Appendix A for a fuller discussion of isochron plots.) The isochron for 12–100% ^{39}Ar release and normalized to ^{37}Ar is shown separately for plag and pyx phases in Fig. 2. This isochron gives a weighted age of 1330 ± 10 Ma and a ^{40}Ar/^{37}Ar intercept of -0.06 ± 0.03. An isochron for 12–100% ^{39}Ar release and normalized to total ^{36}Ar gives an age of 1329 ± 26 Ma and a ^{40}Ar/^{36}Ar intercept of -25 ± 12 (Table 1). Unfortunately, ^{40}Ar and ^{39}Ar, normalized to either ^{36}Ar or ^{37}Ar for those 18 extractions releasing 12–81% of the ^{39}Ar and possessing near-constant K/Ca, show only small variations among extractions and do not define a precise isochron slope or intercept. For example, the isochron for 24–81% ^{39}Ar release and normalized to ^{37}Ar gives an age of 1205 ± 65 Ga and an intercept of 2.8 ± 0.7.

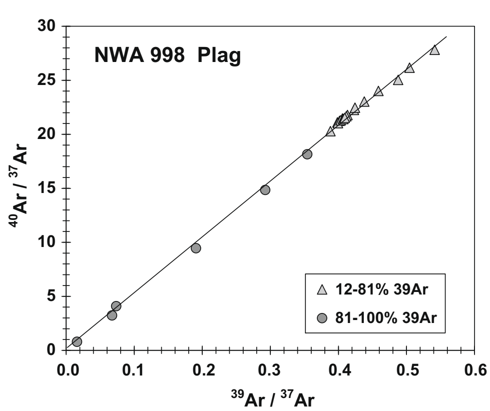

Fig. 2. Isochron plot of ^{40}Ar/^{37}Ar versus ^{39}Ar/^{37}Ar shown separately for extractions releasing 12–81% and 81–100% of the ^{39}Ar from NWA 998 Plag. Individual errors are smaller than the symbols.

The strong linearity of these NWA 998 isochrons ($R^2 \geqslant 0.998$) and near-zero intercepts on the Y-axis indicate that essentially all of the ^{40}Ar is strongly correlated in the lattice with ^{39}Ar and K and results from *in situ* decay (see Appendix A). Because recoil gain of ^{39}Ar in pyroxene ($\sim$81–100% ^{39}Ar release) is included in some of the plotted isochron data, we might expect those isochron ages to be slighter smaller than the age of 1334 ± 11 Ma derived from Fig. 1, and this is observed. From this analysis of Ar–Ar data, we conclude that our NWA 998 sample contained insignificant amounts of trapped ^{40}Ar and probably also ^{36}Ar, and that its preferred Ar–Ar age is 1334 ± 11 Ma.

3.2. NWA 998 CRE age

We analyzed cosmogenic noble gases in a 0.0387 g unirradiated sample of NWA 998 olivine, in order to determine its cosmic-ray exposure (CRE) age. Previous determinations of CRE ages for nakhlites (Eugster et al., 1997; Okazaki et al., 2003; Christen et al., 2004; Murty et al., 2005) suggest they all may have been ejected from Mars at the same time, although the CRE age for NWA 998 has not been reported. We analyzed an olivine separate because its chemical composition has been measured and is relatively uniform (Irving et al., 2002). Measured noble gas concentrations (units 10^{-9} cm^3 STP/g) were: ^{3}He = 192. ^{4}He = 4688, ^{20}Ne = 18.6, ^{21}Ne = 22.4, ^{22}Ne = 26.1, ^{36}Ar = 2.66, ^{38}Ar = 3.98, and ^{40}Ar = 9.24. The ^{3}He is entirely cosmogenic in origin, and the measured ^{21}Ne/^{22}Ne and ^{36}Ar/^{38}Ar ratios of 0.86 and 0.67, respectively, indicate that ^{21}Ne and ^{38}Ar also are entirely cosmogenic.

To calculate CRE ages for NWA 998, we used elemental production rates derived from several sources and summarized by Eugster and Michel (1995). These rates, which are based on composition alone and assume average shielding, give calculated CRE ages of ^{3}He = 12.7 Ma, ^{21}Ne = 10.6 Ma, and ^{38}Ar = 9.3 Ma. Using cosmogenic data obtained on a suite of achondrites, including several diogenites, Eugster and Michel (1995) presented a method to use the measured cosmogenic ^{21}Ne/^{22}Ne ratio to adjust the ^{21}Ne and ^{3}He production rates for differences in shielding. These authors presented only one formula to correct ^{3}He, but three different formulas to correct ^{21}Ne, which were based on results from analyses of eucrites, howardites, and diogenites. For NWA olivine, we used the formula for diogenites, whose composition more resembles olivine than does the compositions of eucrites and howardites. Because NWA 998 olivine contains less Si, Al, and Mg, and more Fe compared to diogenites, it is unclear how accurate elemental production rates derived from these achondrites will be to the production rates in olivine. Using these shielding-corrected production rates the ^{21}Ne and ^{3}He ages become 14.5 Ma and 13.0 Ma, respectively. Using the shielding-corrected production rate derived for howardites, the ^{21}Ne age is 12.2 Ma.

These CRE ages calculated above for NWA 998 are generally similar to analogous CRE ages reported for Nakhla,

Table 1
Nakhlite ages in Ma and isochron intercept ratios obtained by various methods.

Meteorite/ phase	Sloped spectrum	Partial plateau	Total ^{36}Ar isochron	Trap ^{36}Ar isochron	Total ^{37}Ar isochron	Literature Ar–Ar ages	Other ages
NWA 998							1.29 ± 0.05 (a)
Plag Age, Ma		**1334 ± 11**	1329 ± 26	na	1330 ± 10		
Plag ^{40}Ar/^{XX}Ar			−25 ± 12		0.06 ± 0.03		
MIL 03346						1360 ± 2 (e)	1.36 ± 0.03 (b)
WR Age, Ma	1373 ± 105		1434 ± 96 (*1449 ± 8*)	1447 ± 69	na		
WR ^{40}Ar/^{XX}Ar			−1150 ± 1282	−1460 ± 1096			
Meso Age, Ma	1413 ± 88	1365 ± 15	**1368 ± 83** (*1407 ± 9*)	na	na		
Meso ^{40}Ar/^{XX}Ar			697 ± 1525				
Pyx Age, Ma	1404 ± 182	**1334 ± 54**	~1300	na	~1400		
Pyx ^{40}Ar/^{XX}Ar			na		na		
Y-000593						1400 ± 60 (f)	1.31 ± 0.03 (c)
WR Age, Ma	1405 ± 107		1398 ± 246 (*1359 ± 20*)	1394 ± 116	1483 ± 23		
WR ^{40}Ar/^{XX}Ar			598 ± 3192	950 ± 2051	−3.1 ± 0.8		
Plag Age, Ma	1397 ± 91	**1367 ± 7**	na	na	1416 ± 17 (*1434 ± 7*)		
Plag ^{40}Ar/^{XX}Ar			na	na	−1.8 ± 0.8		
Pyx Age, Ma	1416±116		1443±213	na	1410 ± 33		
Pyx ^{40}Ar/^{XX}Ar			3.5 ± 63	na	0.012 ± 0.010		
Nakhla						1323 ± 11 (g)	1.27 ± 0.01 (d)
WR Age, Ma	1390 ± 87	**1357 ± 11**	1356 ± 21		1356 ± 24		
WR ^{40}Ar/^{XX}Ar			11 ± 1496		0.04 ± 0.53		
Lafayette						1330 ± 30 (h) 1332 ± 10 (i)	1.32 ± 0.02 (d)
Governador Valadares						1320 ± 40 (j)	1.33 ± 0.01 (d)

Column 1 gives the meteorite and phase analyzed and indicates whether the values listed are ages or isochron intercepts. Ar–Ar age values given in columns 2 and 3 are averages of the downward sloped portion of the age spectrum or of a partial age plateau, respectively. Ages and isotopic ratios (^{40}Ar/^{XX}Ar) given in columns 4–6 are derived from isochron plots normalized to total ^{36}Ar, trapped ^{36}Ar, or ^{37}Ar, respectively. All uncertainties in age and ^{40}Ar/^{36}Ar intercepts are approximately 2σ. Isochron ages for MIL 03346 Pyx are very approximate. na signifies no meaningful isochron was obtained. Isochron ages in (*italic*) are the same data unweighted by individual uncertainties. Our preferred Ar–Ar ages are indicated in bold. Column labeled Other Ages gives either Sm–Nd isochron ages or preliminary Rb–Sr isochron ages as reported by (a) Carlson and Irving (2004), (b) Shih et al. (2006), (c) Misawa et al. (2005), (d) Nyquist et al. (2001), and references therein. Column labeled literature Ar–Ar ages gives values obtained by other workers: (e) total age, Anand et al., 2006; (f) partial plateau age for Y-000749, paired with MIL 03345, Shankar et al., 2008; (g) partial plateau, Swindle and Olson, 2004; (h) plateau, Podosek, 1973; (i) partial plateau, Swindle and Olson, 2004; (j) plateau, Bogard and Husain, 1977.

Lafayette, and Governador Valadares (Eugster et al., 1997), for MIL 03346 (Murty et al., 2005), and for Y-000593 and its paired nakhlites (Okazaki et al., 2003; Christen et al., 2004). For most reported CRE age determinations of nakhlites, ^{3}He and ^{21}Ne ages are in fair agreement, around 10–13 Ma, whereas the ^{38}Ar ages are somewhat younger. NWA 998 also shows a younger $^{38}Ar_{cos}$ age. Younger ^{38}Ar ages in nakhlites could derive from a bias in the production rate equations for ^{38}Ar as a function of chemical composition, or a bias could be introduced because a shielding correction was not applied to ^{38}Ar. We conclude that the CRE age of NWA 998, like the Ar–Ar age, is similar, possibly identical, to the CRE ages for other nakhlites and thus permits ejection of all nakhlites by a single impact from the same martian locale.

3.3. MIL 03346 Ar–Ar age

The Ar–Ar age spectra for MIL 03346 whole rock (WR), mesostasis (Meso), and pyroxene (Pyx), shown in Figs. 3 and 4, are similar, although the Pyx data have much larger uncertainties because of smaller K and ^{40}Ar concentrations and larger reactor corrections. Except for evidence of diffusive loss of ^{40}Ar in the first few extractions, the apparent ages for WR and Meso decrease steadily throughout the extractions from ~1.52 Ga down to ⩽1.28 Ga. The K/Ca ratios for MIL 03346 WR and Meso samples are constant at ~0.5 through ~80% of the ^{39}Ar release, then show an accelerating decrease. According to Day et al. (2006), K/Ca ratios in Al-rich glass, K–P–Ca-rich glass and silica-rich zones are 0.19–0.78, 0.23–1.04, and 0.23–0.58, respectively. All three of these phases probably contribute to ^{39}Ar in the first ~80% of the ^{39}Ar release. A pyroxene contaminant having a much lower K/Ca ratio contributed to the last ~20% of the ^{39}Ar release in Meso and WR. A portion of the younger age at high temperature releases may be caused by recoiled ^{39}Ar implanted into pyroxene, as this process can become important at finer grain sizes (Huneke and Smith, 1976). The Pyx shows generally similar ages and

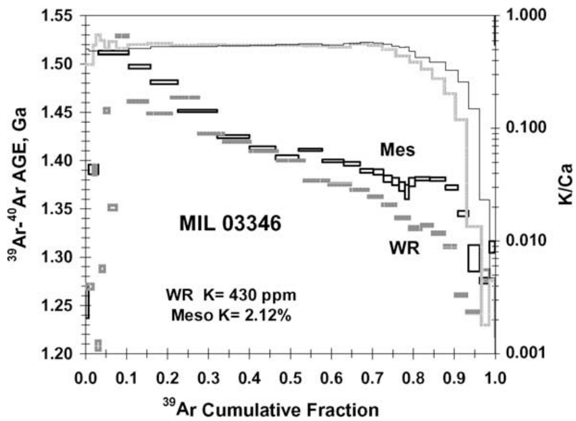

Fig. 3. ^{39}Ar–^{40}Ar ages (rectangles, left *Y*-axis) and K/Ca ratios (stepped lines, right *Y*-axis) for stepwise temperature release of mesostasis and whole rock samples of nakhlite MIL 03346. K concentrations are indicated.

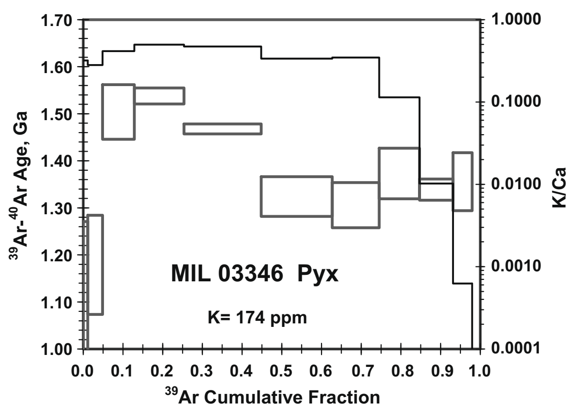

Fig. 4. ^{39}Ar–^{40}Ar ages (rectangles, left *Y*-axis) and K/Ca ratios (stepped lines, right *Y*-axis) for stepwise temperature release of pyroxene from nakhlite MIL 03346. K concentrations is indicated.

K/Ca (Fig. 4) to those of WR and Meso. The relatively high initial K/Ca for the Pyx (∼0.4) indicates that a mesostasis contaminant was the major carrier of K in Pyx. The K/Ca ratio of the pyroxene alone is possibly similar to the ratio of ∼0.001 shown at highest temperature.

For MIL 03346 WR, 17 extractions releasing 10–90% of the ^{39}Ar (nearly constant K/Ca) give an average age of 1373 ± 105 Ma. For the Meso sample, 19 extractions releasing 3–88% of the ^{39}Ar give an average age of 1413 ± 88 Ma. For the Pyx sample, 8 extractions releasing 5–98% of the ^{39}Ar give an age of 1404 ± 182 Ma (Table 1). Both the Meso and Pyx samples suggest limited "plateau" ages (Table 1) of Meso = 1365 ± 15 Ma (9 extractions over 73–91% ^{39}Ar release) and Pyx = 1334 ± 54 Ma (5 extractions over 45–98% ^{39}Ar release). The preliminary Sm–Nd age for MIL 03346 is 1.36 ± 0.03 Ga (Shih et al., 2006), which is similar to most of these Ar–Ar ages and to the total Ar–Ar age reported by Anand et al. (2006).

For MIL 03346, we examined three types of isochron plots (Appendix A) for 17 extractions of the WR releasing 10–90% of the ^{39}Ar, and for 19 extractions of the Meso releasing 3–88% of the ^{39}Ar. These data showed approximately constant K/Ca ratios. Fig. 5 shows these isochrons normalized to total ^{36}Ar. The WR isochron slope yields an age of 1434 ± 96 Ma, and the Meso isochron slope yields an age of 1368 ± 83 Ma. The MIL 03346 WR isochron normalized to trapped ^{36}Ar gives an age of 1447 ± 69 Ma. To calculate the amounts of trapped ^{36}Ar and cosmogenic ^{36}Ar for each extraction, we utilized measured $^{36}Ar_{cos}$ in an unirradiated WR MIL 03346 sample (1.25×10^{-8} cm^3/g; Park, 2005) and the measured $^{36}Ar/^{37}Ar$ ratios for each extraction (Garrison et al., 2000). Because we do not have an independent measure of $^{36}Ar_{cos}$ in MIL 03346 Meso, we cannot construct a Meso isochron normalized to trapped ^{36}Ar. We also examined isochron plots of $^{40}Ar/^{37}Ar$ versus $^{39}Ar/^{37}Ar$. However, for the same extractions as shown in Fig. 5, the isochron plots normalized to ^{37}Ar display much less variation in isotopic ratios and do not define isochron slopes or intercepts. Isochrons for Pyx, normalized to either total ^{36}Ar or ^{37}Ar, are less precise and give "ages" of ∼1.3 Ga and ∼1.4 Ga, respectively (Table 1).

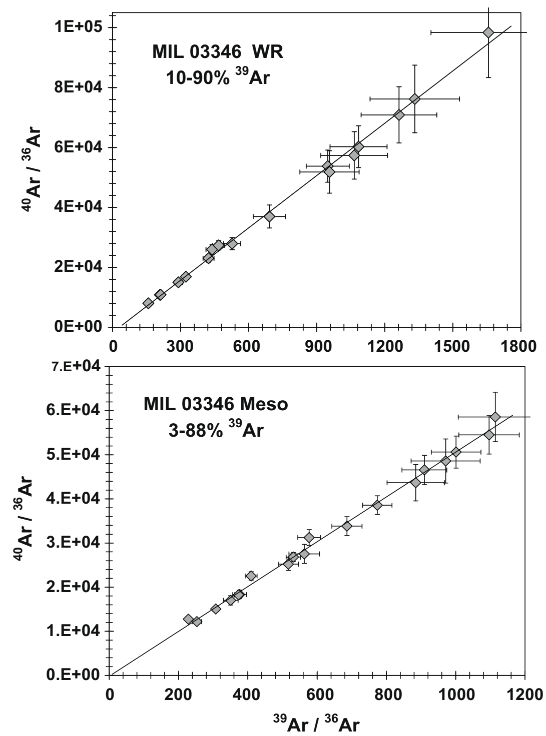

Fig. 5. Isochron plot of $^{40}Ar/^{36}Ar$ versus $^{39}Ar/^{36}Ar$ for extractions releasing 10–90% of the ^{39}Ar from MIL 03346 whole rock (top) and for extractions releasing 3–88% of the ^{39}Ar from MIL 03346 mesostasis (bottom). Total ^{36}Ar is used for normalization. Errors not indicated are contained within the symbols.

3.4. Y-000593 Ar–Ar

The Ar–Ar age spectra for Y-000593 whole rock (WR), plagioclase (Plag), and pyroxene (Pyx) are shown in Figs. 6 and 7. We previously reported the Ar–Ar data for

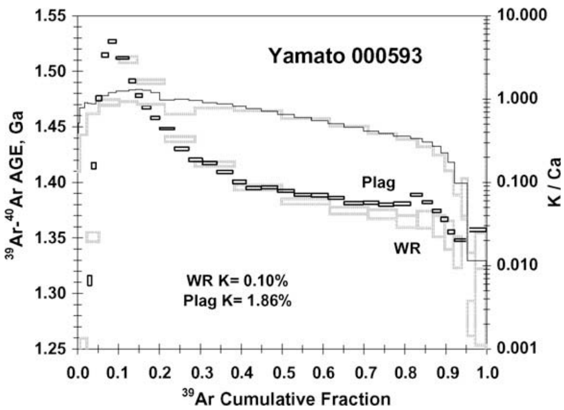

Fig. 6. ^{39}Ar–^{40}Ar ages (rectangles, left *Y*-axis) and K/Ca ratios (stepped line, right *Y*-axis) for stepwise temperature release of whole rock and plagioclase samples of nakhlite Y-000593. Determined K concentrations are indicated.

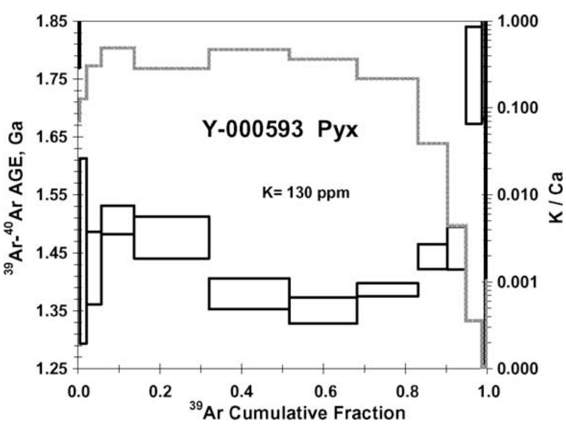

Fig. 7. ^{39}Ar–^{40}Ar ages (rectangles, left *Y*-axis) and K/Ca ratios (stepped line, right *Y*-axis) for stepwise temperature release of a pyroxene sample of nakhlite Y-000593.

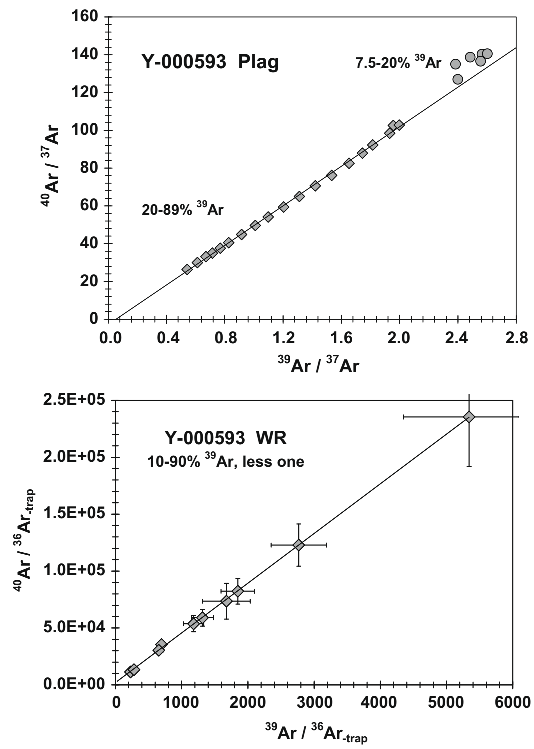

Fig. 8. (Top) Isochron plot of $^{40}Ar/^{37}Ar$ versus $^{39}Ar/^{37}Ar$ for extractions releasing 20–89% of the ^{39}Ar and 7.5–20% of the ^{39}Ar from a plagioclase sample of Y-000593. (Bottom) Isochron plot of $^{40}Ar/^{36}Ar_{trap}$ versus $^{39}Ar/^{36}Ar_{trap}$ for extractions (except one) releasing 10–90% of the ^{39}Ar from Y-000593 whole rock. Individual errors not indicated are contained within the symbols.

Y-000593 WR (Misawa et al., 2005). Overall, these age spectra are similar to those presented for MIL 03346. The first ~10% of the ^{39}Ar release for the WR and Plag samples show some diffusive loss of ^{40}Ar, and recoil of ^{39}Ar into a pyroxene phase is obvious above ~90% ^{39}Ar release. With increasing extraction temperature, the WR and Plag ages decrease steadily from a high of $\geqslant 1.5$ Ga down to ~1.30 Ga. The K/Ca ratios for the WR and Plag decrease steadily from a value of ~1 at low temperatures to a value of ~0.3 at 85% ^{39}Ar release, then decrease more rapidly as pyroxene degases Ar. The Pyx separate shows a K/Ca of ~0.3 for the first ~80% of the ^{39}Ar release, then decreases to $\leqslant 0.001$, indicating that most K in Pyx resided in a plagioclase contaminant. Imae and Ikeda (2007) reported that K/Ca in Y-000593 mesostasis is about 0.62, while Treiman (2005) reported that K/Ca ratios in Y-000593 plagioclase and Y-000593 alkali feldspar as 0.09 and 17.44, respectively. Our Plag mineral separate for Y-000593 is a mixture of mesostasis and plagioclase with minor alkali feldspar. The average Ar–Ar age for 13 extractions of the WR sample, releasing 10–90% of the ^{39}Ar, is 1405 ± 107 Ma. The average Ar–Ar age for 25 extractions of the Plag, releasing 7.5–89% of the ^{39}Ar, is 1397 ± 91 Ma. The average Ar–Ar age for 7 extractions of the Pyx, releasing 6–95% of the ^{39}Ar, is 1416 ± 116 Ma (Table 1). Four Plag extractions (65–82% ^{39}Ar) give a "plateau" age of 1367 ± 7 Ma. The Sm–Nd and Rb–Sr isochron ages reported for Y-000593 are 1.31 ± 0.03 Ga and 1.30 ± 0.02 Ga, respectively (Misawa et al., 2005). For Y-000749, which is paired with Y-000593, Shankar et al. (2008) give an average Ar–Ar age of 1.40 ± 0.06 Ga and an isochron age of 1.38 ± 0.10 Ga.

An isochron for 10–90% ^{39}Ar release of Y-000593 WR, normalized to total ^{36}Ar, gives an imprecise age of 1398 ± 246 Ma, and an isochron normalized to ^{37}Ar gives an older age of 1483 ± 23 Ma (Table 1). An isochron normalized to trapped ^{36}Ar (Fig. 8) gives an age of 1394 ± 116 Ma. To calculate trapped ^{36}Ar, we first utilized measurements of cosmogenic ^{36}Ar (1.07×10^{-8} cm^3/g) reported by Okazaki et al. (2003) for unirradiated whole rock samples to apportion the ^{36}Ar for each extraction between cosmogenic and trapped components. However, this $^{36}Ar_{cos}$ value caused a few of the $^{36}Ar/^{37}Ar$ ratios to be negative, indicating that we overcorrected for $^{36}Ar_{cos}$. Thus, we utilized the minimum measured $^{36}Ar/^{37}Ar$ ratio to apportion the ^{36}Ar for each extraction between cosmogenic and trapped components. This gave a slightly lower cosmogenic ^{36}Ar concentration of 0.98×10^{-8} cm^3/g.

Isochron data for 7.5–89% ^{39}Ar release of the Plag, normalized to ^{37}Ar, are shown in Fig. 8. Ratios for extractions releasing 20–89% of the ^{39}Ar are strongly linear and give a weighed age of 1416 ± 17 Ma and an unweighed age of 1434 ± 7 Ma (Table 1). Extractions releasing 7.5–20% of the ^{39}Ar cluster above this isochron. Unfortunately, due to a variable background at mass 36 and small ^{36}Ar signals, the Y-000593 Plag sample did not give accurate ^{36}Ar measurements. For the Y-000593 Pyx sample, an isochron over 0.5–95% ^{39}Ar release and normalized to total ^{36}Ar gives an age of 1443 ± 213 Ma. An isochron of the same data normalized to ^{37}Ar gives an age of 1410 ± 33 Ma (Table 1). Comparison of apparent Ar–Ar ages at higher temperatures in Figs. 4 and 7, where pyroxene degassed, indicate that Y-000593 Pyx contained greater amounts of trapped ^{40}Ar than did MIL 03346 Pyx.

3.5. Nakhla Ar–Ar

The Ar–Ar age spectrum for Nakhla WR (Fig. 9) shows an age peak at ~1.47 Ga, followed by an apparent age plateau over ~41–91% ^{39}Ar release, then decreasing ages. Some ^{40}Ar diffusive loss likely occurred below 11% ^{39}Ar release, and the age decrease above 91% ^{39}Ar release is probably gain of recoiled ^{39}Ar by pyroxene. The average age of extractions releasing 41–91% of the ^{39}Ar is 1357 ± 11 Ma (2σ). The average age across 7–91% ^{39}Ar release is 1390 ± 87 Ma (Table 1).

An isochron plot for Nakhla WR, normalized to ^{37}Ar for extractions releasing 7–91% of the ^{39}Ar, is shown in Fig. 10. Extractions releasing 41–91% of the ^{39}Ar define a precise (weighted) isochron age of 1356 ± 24 Ma and a $^{40}Ar/^{37}Ar$ intercept of 0.04 ± 0.53 (Table 1). The same data normalized to total ^{36}Ar give a weighted age of 1356 ± 21 Ma and a $^{40}Ar/^{36}Ar$ intercept of 11 ± 1496. The observations that these two isochron ages are identical to the plateau age and that the ^{40}Ar axis intercepts are within error of zero, suggest that significant excess ^{40}Ar was not present in extractions releasing 41–91% of the ^{39}Ar. Our preferred Ar–Ar age for Nakhla is 1357 ± 11 Ma (2σ).

Those extractions releasing 7–41% of the ^{39}Ar and normalized to ^{37}Ar cluster above the isochron in Fig. 10 and do not define a slope or intercept. We utilized the minimum measured $^{36}Ar/^{37}Ar$ ratio to apportion the ^{36}Ar into trapped and cosmogenic components for extractions releasing 7–41% of the ^{39}Ar. Because measured $^{36}Ar/^{37}Ar$ for these extractions are much higher than the minimum ratio, this process is not sensitive to the total $^{36}Ar_{cos}$ present. An isochron for these extractions normalized to trapped ^{36}Ar also is shown in Fig. 10. The unweighted isochron slope gives an age of 1391 ± 41. If we weigh each ratio in the isochron by its uncertainty (Williamson, 1968), the age becomes 1465 ± 134 Ma and the intercept becomes -422 ± 2548. Although this analysis suggests extractions releasing 7–41% of the ^{39}Ar also released an excess ^{40}Ar component, the possibility of recoil loss of ^{39}Ar for these extractions cannot be completely ruled out.

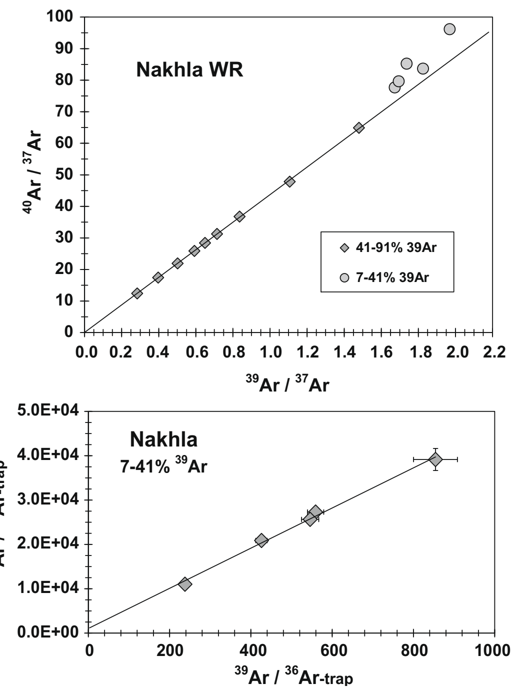

Fig. 10. (Top) Isochron plot of $^{40}Ar/^{37}Ar$ versus $^{39}Ar/^{37}Ar$ shown separately for extractions releasing 41–91% and 7–41% of the ^{39}Ar from Nakhla whole rock. (Bottom) Isochron plot of $^{40}Ar/^{36}Ar_{trap}$ versus $^{39}Ar/^{36}Ar_{trap}$ for extractions releasing 7–41% of the ^{39}Ar released from Nakhla whole rock. Most individual errors are contained within the symbols.

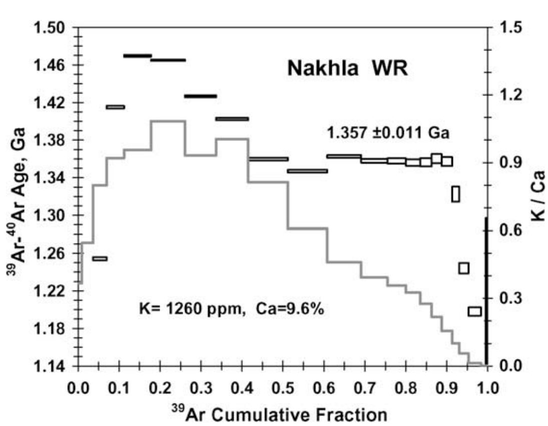

Fig. 9. ^{39}Ar–^{40}Ar ages (rectangles, left Y-axis) and K/Ca ratios (stepped line, right Y-axis) for stepwise temperature release of Nakhla whole rock. Determined K and Ca concentrations are indicated.

4. DISCUSSION

4.1. Other nakhlite samples

Several workers have reported Ar–Ar analyses for whole rock and mineral samples of Nakhla and Lafayette (Podosek, 1973; Gilmour et al., 1998; Burgess et al., 2000; Swindle and Olson, 2004). The Ar–Ar age spectra for Nakhla measured by Burgess et al. (2000) and Gilmour et al. (1998) show small or no age peaks at low extraction temperatures, broad age plateaus, and small ^{39}Ar recoil effects at high temperatures. Age spectra reported by Swindle and Olson (2004) for both Nakhla and Lafayette did show significantly higher ages at lower extraction temperatures, a quasi-plateau in age at intermediate temperatures, and gain of recoiled ^{39}Ar at high extraction temperatures, much like Fig. 9. The age spectrum for Governador Valadares is relatively flat (Bogard and Husain, 1977). An Ar–Ar age spectrum of Y-000749, paired with Y-000593, shows a higher age peak at lower extraction temperature and a broad plateau age of 1.40 ± 0.06 Ga (Shankar et al., 2008). Anand et al. (2006) did not present an age spectra for MIL 03346, and Gilmour et al. (1998) and Burgess et al. (2000) did not give Ar–Ar ages for their Nakhla data. Swindle and Olson (2004), utilizing only those extractions showing similar ages, derived Ar–Ar ages of 1332 ± 10 and 1323 ± 11 Ma for their two Nakhla samples and 1322 ± 10 Ma for Lafayette. (Whether these age uncertainties represent 1σ or 2σ was not stated.) It is not clear why the plateau ages reported by Swindle and Olson (2004) are 24–34 Ma younger than the Nakhla age we report here, but the difference likely is related to whatever produces the downward sloped age spectra. In accounting for higher ages at lower extraction temperatures, Swindle and Olson (2004) favored redistribution of ^{39}Ar by recoil during neutron irradiation, possibly from the secondary mineral iddingsite. However, this explanation would imply that about half of the K resides in iddingsite (Fig. 9), which seems excessive. The observation that some reported Ar–Ar age spectra of nakhlites display high temperature ^{39}Ar recoil effects, but little to no age peaks at low extraction temperatures, suggests that these age peaks may not be primarily produced by ^{39}Ar recoil loss, but rather are intrinsic to the samples.

4.2. Cause of downward sloped age spectra

There are two conceivable explanations for the downward sloping age spectra shown by all analyzed samples of MIL 03346, Y-000593, and Nakhla reported here and by some nakhlite samples reported in the literature. First, the slope may have been produced as a result of K-bearing phases having relatively small grain size and ^{39}Ar recoil effects during irradiation having modified the entire age spectrum. Thus, the highest ages observed in the downward sloping portion of the age spectra would occur because of ^{39}Ar recoil loss and the lowest ages in the downward sloping portion would occur because of gain of recoiled ^{39}Ar. Conceivably, the correct Ar–Ar age might be given by the weighted average of those ages defining the sloped age spectra. The second possible explanation for the downward sloping spectra is that these nakhlite samples contain trapped terrestrial atmospheric ^{40}Ar or martian ^{40}Ar, not arising from *in situ* decay (Bogard and Johnson, 1983; Walton et al., 2007; Bogard and Park, 2008), and released primarily at lower temperatures. Trapped martian atmospheric noble gases have been measured in MIL 03346 (Murty et al., 2005; Nagao and Park, 2008) and in other nakhlites (Drake et al., 1994; Gilmour et al., 2001), and at least some of these excess noble gases seem to be associated with martian weathering products (Drake et al., 1994; Swindle et al., 2000). Other workers have demonstrated that noble gases can be incorporated from the terrestrial atmosphere into martian meteorites, including nakhlites, and these may mimic a martian component (Hermann et al., 2006; Schwenzer et al., 2007; Ott, 2008). To evaluate these two possible explanations for downward sloped age spectra, we further consider the isochron plots for our data (also see Appendix A).

4.2.1. MIL 03346 and Y-000593

The isochron plots for MIL 03346 give variable Ar intercept ratios (Table 1), mostly within error of zero, but uncertainties are large. However, the WR sample suggests negative intercepts. A negative intercept could be produced by recoil, or alternatively, if the trapped $^{40}Ar/^{36}Ar$ ratio released from the WR changed with extraction temperature. In fact, it is those lower temperature WR extractions with higher $^{40}Ar/^{36}Ar$ ratios that primarily control the isochron slope, whereas ^{37}Ar and cosmogenic ^{36}Ar are primarily released at higher temperatures and these ratios plot closer to the origin. Thus, if excess ^{40}Ar was primarily correlated with grain surfaces, as could be expected with either adsorbed terrestrial Ar or a martian atmospheric component introduced by grain weathering, then the isochrons could be rotated toward older ages and negative intercepts. From this effect, we would expect the actual Ar–Ar ages to be lower than these isochron ages.

We give the following interpretation of the Ar–Ar age spectra for MIL 03346. Reactor recoil of ^{39}Ar undoubtedly affected those ages shown by the first $\sim$10% and last $\sim$10% of the ^{39}Ar release. Those ages calculated from 10% to 90% of the ^{39}Ar release may have been slightly increased by degassing of martian or terrestrial atmospheric ^{40}Ar from grain surfaces at lower temperatures and possibly by some ^{39}Ar redistribution by recoil. If similar amounts of excess ^{40}Ar are present in WR and Meso, their effect on the age should be much less noticeable in Meso, because Meso has a much higher K concentration (2.1%) compared to the WR (430 ppm). Yet, the age for Meso determined from the downward sloped portion of the spectrum is higher than that for WR. Normally, we would suggest that the preferred Ar–Ar age for MIL 03346 is given by the 1365–1368 Ma "plateau" age and isochron age for Meso. However, the Pyx age of 1334 ± 54 is lower, although within uncertainties of the Meso age. Although relatively uncertain, these Ar–Ar ages agree with the preliminary Sm–Nd age of 1.36 ± 0.03 Ga (Shih et al., 2006) and with the more precise Ar–Ar age for NWA 998 (Table 1).

Although some Y-000593 isochron intercepts are uncertain, some suggest intercept ratios close to zero or slightly negative (Table 1). Again, a negative intercept could indicate that the isochron has been rotated, either by Ar recoil redistribution or by release of excess ^{40}Ar at lower extraction temperatures, and that the isochron ages have been artificially increased. If Plag and WR contain similar amounts of excess ^{40}Ar, its effect should be greater on the WR age (K = 0.10%) than on the Plag age (K = 1.86%). Thus, we prefer the youngest Plag "plateau" age of 1367 ± 7 Ma, although it is derived from a limited portion of the ^{39}Ar release. This age overlaps, within relative uncertainties, the preferred Ar–Ar ages for NWA 998 and MIL 03346, but it is slightly older than the Y-000593 Sm–Nd isochron age of 1.31 ± 0.03 Ga (Misawa et al., 2005).

4.2.2. Effects of grain size versus martian weathering

Given the finer grain size of MIL 03346 compared to other nakhlites (see EA-1), we might expect it to show larger recoil effects. A finer grain size for MIL 03346 also is evident in Arrhenius plots of the Ar diffusion parameter, D/a^2, as a function of reciprocal temperature for feldspathic separates of these four nakhlites (Fig. 11). Higher values of D/a^2 for Ar diffusion in MIL 03346 Meso exist at all temperatures compared to NWA 998 Plag, Y-000593 Plag, Nakhla WR, and Zagami shergottite Plag. (See Bogard and Park, 2008, for Zagami Arrhenius plot and explanation of how we calculate Ar diffusion data.) This is additional evidence that the size of K-containing grains is smaller in MIL 03346, and thus it should be more easily affected by ^{39}Ar recoil. NWA 998, with a relatively coarse grain size (EA-1), does not show a downward sloped age spectrum, whereas the other three nakhlites do. Also, Plag from the Zagami shergottite, which shows generally similar Ar diffusion characteristics to three of these nakhlites (Fig. 11), does not show obvious ^{39}Ar recoil effects. If, as expected, ^{39}Ar recoil effects increase with decreasing grain size, one might expect MIL 03346 to show the greatest recoil effect, NWA 998 the least, and Nakhla and Y-000593 similar, intermediate effects. Further, if the downward sloped spectra were entirely produced by ^{39}Ar recoil, one might expect a greater age decrease for the pyroxene contaminants in the WR and Meso/Plag samples, compared to what is observed. The observation that the downward sloped portion of the age spectra give ages older than other radiometric chronometers would have to imply that part of the ^{39}Ar recoiled out of the rocks. We conclude, therefore, that ^{39}Ar recoil probably has occurred in these nakhlite analyses but cannot be the full explanation of all the observed sloped age spectra. It also is unlikely that differences in shock levels generated this difference in Ar diffusion, and we point out that Ar diffusion in shergottites, with higher shock levels than nakhlites, is well behaved (Bogard, 2009).

At least part of the downward sloped age spectra likely resulted from adsorbed martian or terrestrial atmosphere preferentially released at lower extraction temperatures (see Section 4.2). The observation that NWA 998 and some other nakhlite analyses reported in the literature (Table 1) did not release excess ^{40}Ar would imply such a component is variable among samples. Excess Ar in shergottites originating from shock-implanted atmosphere and trapped from the magma is commonly released at higher extraction temperatures (Bogard and Garrison, 1999; Bogard and Park, 2008). If, however, excess ^{40}Ar in nakhlites was adsorbed on surfaces of grains weathered in the martian environment (Drake et al., 1994; Gilmour et al., 2001) or the terrestrial environment (Schwenzer et al., 2007), then one would expect it to release at lower temperatures. If this excess ^{40}Ar does represent martian atmosphere in weathered phases, it apparently is concentrated in feldspathic phases over pyroxene. The Pyx samples of MIL 0346 and Y-000593 contain much less K, yet show similar apparent Ar–Ar ages at low temperature compared to the feldspathic and WR phases. It is not obvious why martian atmosphere should be preferentially concentrated in weathered feldspar over weathered pyroxene. However, Gilmour et al. (1999) reported martian atmospheric Xe in Nakhla to occur in higher concentrations in mesostasis compared to mafic

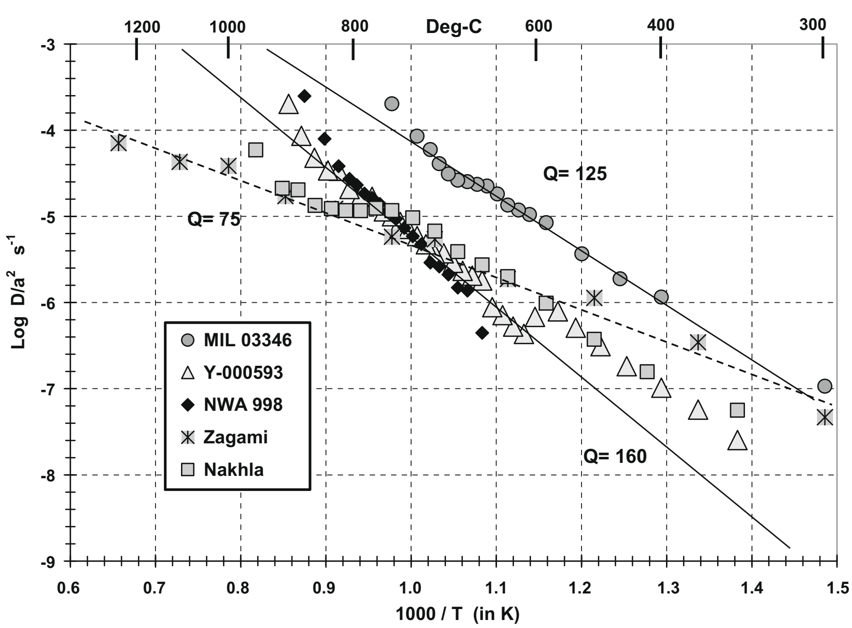

Fig. 11. Arrhenius diffusion plot of log D/a^2 versus reciprocal temperature (in K) of ^{39}Ar in four nakhlites and the Zagami shergottite (dashed line). Data from higher temperature extractions of the nakhlites have not been included in these calculations, nor have data from low-temperature extractions of NWA 998. Calculated activation energies (Q in kJ/mole) are shown for the linear trends defined by MIL 03346, Y-000593, and Zagami data. Ar diffusion from MIL 03346 is considerably faster than from the other three nakhlites and Zagami, indicating smaller grains sizes for K-bearing phases.

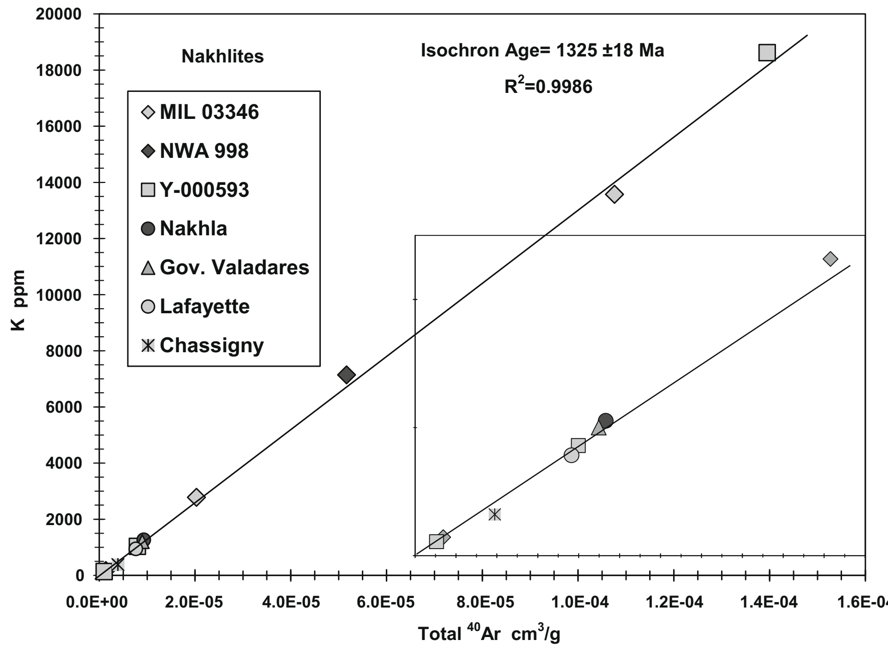

Fig. 12. Isochron of K concentration (ppm) versus total ^{40}Ar concentration (cm^3 STP/g) for whole rock and mineral separates of six nakhlites (this work, Podosek, 1973; Bogard and Husain, 1977) and the Chassigny dunite (Bogard and Garrison, 1999). The inset graph in the lower right reproduces those data having K concentrations <3000 ppm. In terms of K concentrations, feldspathic separates are highest, pyroxene separates are lowest, and whole rock samples are intermediate. Collectively, the data define an age of 1325 ± 18 Ma.

minerals. Thus, the detailed explanation for downward sloped Ar–Ar age spectra in some nakhlites remains something of an enigma.

4.3. K–^{40}Ar isochron age of six nakhlites

The JSC laboratory has reported ^{39}Ar–^{40}Ar data for five nakhlites. In Fig 12 we show an isochron plot of total ^{40}Ar versus total K for all these data, including whole rock and mineral separates. These absolute concentrations typically are measured less precisely than the isotopic ratios utilized in the Ar–Ar isochrons presented above. Thus, to minimize inter-laboratory bias in calibrating absolute concentrations, it is desirable to utilize K–Ar data from a single laboratory. Further, some other laboratories did not report K concentrations for the same samples as Ar–Ar determinations. However, to present a larger data set we also plot data for a sixth nakhlite, Lafayette (Podosek, 1973), and for comparison, JSC data for the Chassigny dunite, whose age is known to be similar to those of the nakhlites (Nyquist et al., 2001). The unweighted K–Ar isochron age for all data of the six nakhlites is 1325 ± 18 Ma (2σ; $R^2 = 0.9986$). The intercept on the ^{40}Ar axis for this isochron is $-1 \pm 8 \times 10^{-7}$. If we force the isochron through zero, the age decreases by only 2 Ma. The isochron slope and age primarily are determined by the more radiogenic feldspathic separates of Y-000593, MIL 03346, and NWA 998, but whole rock data for the other three nakhlites, Nakhlite, Lafayette, and Governador Valadares, are equally consistent with the isochron. The isochron age for only those four nakhlite samples showing the highest K concentration is 1333 ± 55 Ma, and the ^{40}Ar intercept is $-1 \pm 4 \times 10^{-6}$. Data for the Chassigny dunite also plots close to the nakhlite isochron. Unlike Ar–Ar ages, the accuracy of this K–^{40}Ar isochron age depends on the accuracy of absolute calibrations of K and ^{40}Ar concentrations. However, the precision of the isochron (±18 Ma) depends much less on concentration determinations than does the absolute age. It is a reasonable measure of the degree to which these six nakhlites all have the same or similar age.

5. CONCLUSIONS

Our preferred Ar–Ar ages for these nakhlites are: NWA 998 = 1334 ± 11 Ma; MIL 03346 either 1368 ± 83 Ma (mesostasis) or 1334 ± 54 Ma (Pyx); Y-000593 = 1367 ± 7 Ma; and Nakhla = 1357 ± 11 Ma (Table 1). Three of these ages are slightly older than Sm–Nd and Rb–Sr ages reported by other labs for these meteorites (Table 1), although for NWA 998 and MIL 03346 the Ar–Ar ages are within uncertainties of these other ages. Because of obvious weathering and ^{39}Ar recoil effects at low and high ^{39}Ar fractional releases, respectively, these preferred Ar–Ar ages were determined from only the intermediate ^{39}Ar releases.

Downward sloping age spectra shown by all analyzed samples of MIL 03346, Y-000593, and Nakhla reported here and by some nakhlite samples reported in the literature likely were produced either by ^{39}Ar recoil effects involving relatively small K-bearing grains, or by adsorbed martian or terrestrial atmospheric ^{40}Ar preferentially released at lower extraction temperatures, or a combination of these two effects. Positive isochron intercepts imply excess ^{40}Ar, and suggestions of negative intercepts for some isochron plots could be consistent with either recoil or trapped ^{40}Ar. Smaller grain size and greater ease of radiogenic Ar diffusion in MIL 03346 compared to other nakhlites would predict greater ^{39}Ar recoil effects. Yet, Y-000593 and Nakhla, with coarser grains, show similar downward sloped age spectra as MIL 03446, and Pyx separates do not show the greater ^{39}Ar recoil effects that might be expected. Thus, we conclude recoil cannot be the complete explanation for the observed downward sloped age spectra.

The likely presence of trapped martian or terrestrial atmospheric ^{40}Ar on weathered grain surfaces and its release at low ^{39}Ar fractional degassing is probably the major explanation of the downward sloped Ar–Ar age spectra. Nakhlites are known to have undergone some martian weathering (Mikouchi et al., 2003; Stopar et al., 2005). The Ar–Ar age one obtains on nakhlites may depend on the amount of excess ^{40}Ar in a given sample and on which portion of the age spectrum is used to derive the age. Our preferred Ar–Ar ages for MIL 03446, Y-000593, and Nakhla should be close to their actual formation times, but we cannot rule out the possibility that trapped ^{40}Ar has made these ages appear very slightly too old.

Do the nakhlites all have the same formation age, or can a case be made for age differences? The maximum spread in previously reported radiometric ages for nakhlites is about ~0.2 Ga (Nyquist et al., 2001; Table 1). Among both Ar–Ar ages and ages obtained by other chronometers, there is a significant grouping around 1.33 Ga. However, our preferred Ar–Ar age for MIL 03346 is 1334 ± 54 to 1368 ± 83, and the preliminary Sm–Nd age is 1.36 ± 0.03 Ga (Shih et al., 2006). From these data it is not clear whether MIL 03346 actually formed earlier than the others. Based on the discussion in Section 4, any Ar–Ar age derived from complex, downward sloping age spectra is difficult to quantify and should be viewed with some caution. The whole rock, K–^{40}Ar isochron age of 1325 ± 18 for six nakhlites (Fig. 12) is consistent with the observed nakhlite age grouping around 1.33 Ga, and the relatively small uncertainty on this K–^{40}Ar age might indicate that all six nakhlites have similar, if not identical formation ages. Our preferred Ar–Ar ages for nakhlites analyzed here (Table 1) tend to agree with this whole rock isochron age, within combined uncertainties. However, given the probability that some Nakhlite data plotted in Fig. 12 may contain small amounts of trapped martian ^{40}Ar, it is not clear why the whole rock isochron should give a relatively precise age, when individual isochrons of some specific meteorites give much more variable ages. We suggest it to be very likely that all nakhlites formed at the same or nearly the same time, and that complexities in some Ar–Ar data make precise ages difficult to measure. The indistinguishable cosmic-ray exposure ages of nakhlites also suggest that they were ejected from a common location on Mars in a single impact.

ACKNOWLEDGMENTS

We thank Tony Irving for the mineral separates of NWA 998, the Antarctic Meteorite Working Group for the sample of MIL 03346, the Japanese Institute for Polar Research for the sample of Y-000593, and Monica Grady and The British Museum for the sample of Nakhla. We thank Chi-Yu Shih for aiding in mineral separation of MIL 03346 and Y-000593. We appreciate review comments by L. Nyquist, G. Herzog, E. Walton, V. Fernandes, and U. Ott.

APPENDIX A. INTERPRETING ISOCHRON PLOTS

In isochron plots of terrestrial samples, ^{40}Ar and ^{39}Ar are normalized to total ^{36}Ar. However, in martian meteorites, both cosmogenic ^{36}Ar and trapped martian ^{36}Ar can be present, and the existence of two uncorrelated ^{36}Ar components can produce scatter in an isochron plot. Two alternatives to using total ^{36}Ar are to separate ^{36}Ar into cosmogenic and trapped components and normalize to one of these, or to normalize ^{40}Ar and ^{39}Ar to ^{37}Ar. Argon-37 is a single component produced in the reactor from Ca. In nakhlites, and especially in plagioclase separates, cosmogenic ^{36}Ar also is mainly produced from Ca and thus is largely distributed through the mineral lattice in association with ^{37}Ar (Bogard and Park, 2008). In addition, the ^{37}Ar concentrations in most of these nakhlite samples are much larger than the ^{36}Ar concentrations, so the uncertainties in measuring the ^{40}Ar/^{37}Ar ratios are considerably smaller than those for the ^{40}Ar/^{36}Ar ratios. To separate total ^{36}Ar into trapped and cosmogenic components, we utilize the ^{36}Ar/^{37}Ar ratios and either assume the minimum ratio represents only $^{36}Ar_{cos}$ or use a direct measurement of $^{36}Ar_{cos}$ in a non-irradiated sample (Garrison et al., 2000). This method has some inherent uncertainties, and even $^{36}Ar_{cos}$ measured in unirradiated samples in different laboratories show significant variations. Unless a meteorite sample contains a significant, easily resolvable component of trapped ^{36}Ar, we prefer to use ^{37}Ar for normalization. However, if a mineral phases shows a constant K/Ca ratio, then normalization to ^{37}Ar in an isochron plot may not give sufficient spread to determine the isochron slope.

A positive intercept in an isochron plot suggests that trapped ^{40}Ar is present. A zero intercept suggests that any trapped ^{40}Ar is significantly smaller than ^{40}Ar resulting from *in situ* decay and that significant ^{39}Ar recoil redistribution has not occurred. A negative intercept (i.e., for MIL 03346 WR) cannot represent a real trapped Ar component. Negative intercepts can result from ^{39}Ar recoil redistribution if Ar degasses at different temperatures from phases with different K/Ca ratios, and this situation can rotate the isochron counter-clockwise toward older ages.

The isochron slopes and ages presented here were calculated by weighting each plotted point by the analytical uncertainties in its isotopic ratios, using the method of Williamson (1968), and reported errors are 2σ. Most of the uncertainties in the individual plotted points derive from ^{36}Ar measurements, when that is the normalizing isotope, whereas the isochron slope yielding the age is determined only by the ^{40}Ar/^{39}Ar ratios, which have much smaller uncertainties. Thus, for three cases in Table 1 we also give in italics the isochron ages for WR and Meso samples using an unweighted fit. In two out of three such cases, although the age uncertainties are smaller than for the weighted fits, the unweighted ages still appear too old.

APPENDIX B. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2008.12.027.

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