**$^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of supergene K-bearing sulfate
minerals: Cenozoic continental weathering and its paleoclimatic
significance in the Tu-Ha Basin, northwestern China**

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Abstract

$^{40}\text{Ar}/^{39}\text{Ar}$ incremental-heating analyses of supergene jarosite and yavapaiite
were conducted for three weathering profiles at the Hongsha, Liuhuangshan, and
Caihuagou deposits in the Tu-Ha Basin. The analyses provide numerical constraints
on the timing and duration of weathering and supergene enrichment. Well-constrained
plateau ages and best-fitting inverse isochrons yield $^{40}\text{Ar}/^{39}\text{Ar}$ ages ranging from

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33.3±0.5 Ma to 3.3±0.4 Ma (1σ). Our $^{40}\text{Ar}/^{39}\text{Ar}$ ages, combined with the published ages, indicate that a protracted history of weathering and supergene enrichment and, by inference, arid-semiarid climate (with at least a moderate amount of precipitation (>10 cm/y)) favorable to intense chemical weathering emerged at 33.3 Ma, 27.7-23.3 Ma, and 16.4-14.7 Ma, and prevailed from 11-7.8 Ma. Then, a progressive change from arid-semiarid towards hyperarid conditions and predominantly hyperarid conditions may have persisted since at least ca. 3.3 Ma. The climatic implications inferred from the weathering geochronology are in agreement with the chemical parameters and isotopic compositions of the Cenozoic sedimentary sequence from the Lianmuqin section in the Tu-Ha Basin, attesting to the reliability of weathering geochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ method as an indicator of paleoclimate in arid areas. Our results suggest that the retreat of the Paratethys Sea, which would have reduced eastward water vapor transport by the westerlies to the Tu-Ha Basin, led to its aridification in the Oligocene and that increased rain shadow effects, resulting from uplift of the Tibetan Plateau and Tian Shan Mountains, played important roles in the aridification history of the Tu-Ha Basin since the late Miocene.

Keywords: weathering; $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology; supergene K-bearing sulfates; Tulufan-Hami Basin; aridification

Introduction

Weathering profiles record a balance between weathering and erosion

processes in the geomorphologic and geochemical evolution of the earth's surface (Tardy and Roquin, 1992; Thomas, 1994; Vasconcelos, 1999a). Supergene minerals are formed via weathering processes as thick covers on continents when chemical-physical weathering overwhelms chemical-physical erosion, and thick, chemical and mineralogical weathering profiles develop (Thomas, 1994; Vasconcelos, 1999a). The depth and complexity of weathering profiles, combined with the preservation of supergene minerals throughout the profile, could constitute a long-term record of past climate evolution (Thomas, 1994; Vasconcelos, 1999a). Precise dating and geochemical investigation of supergene minerals may provide important information on the paleoclimatic conditions prevailing during weathering (Alpers, 1988; Vasconcelos, 1999a).

The potassium-bearing alunite-group sulfates (generalized composition $AB_3(SO_4)_2(OH)_6$, jarosite- $KFe_3(SO_4)_2(OH)_6$ and alunite- $KAl_3(SO_4)_2(OH)_6$) are ubiquitous alteration products in supergene profiles developed over sulfide ore deposits and porphyry Cu deposits (Anderson, 1982; Vasconcelos, 1994, 1999b). Vasconcelos et al. (1994) applied laser step heating $^{40}Ar/^{39}Ar$ geochronology to study weathering profiles from the western US and West Africa, demonstrating that supergene jarosite and alunite are suitable minerals for direct dating. The formation of alunite group minerals in weathering profiles requires a balance between (1) depression of the water table by tectonically induced uplift or denudation, and the resultant exposure of underlying sulfides to the effects of oxidative weathering, and (2) an arid-semiarid climate (at least moderate precipitation >10 cm/y) (Clark et al., 1990).

64 However, because jarosite and alunite may be unstable when exposed to saline
65 groundwater; the preservation of jarosite-alunite in weathering profiles is interpreted
66 to record a transition toward arid conditions (Vasconcelos, 1999a). Therefore,
67 $^{40}\text{Ar}/^{39}\text{Ar}$ dating of supergene alunite-group minerals represent a good paleoclimatic
68 indicator and have been used as such in several studies, mainly from the Atacama
69 Desert of Northern Chile and Peru (Alpers et al., 1988; Clark et al., 1990; Sillitoe et
70 al., 1996; Mote et al., 2001; Bouzari et al., 2002; Quang C X et al., 2003, 2005;
71 Araibia et al., 2006), North America (Arehart et al., 1992; Rye et al., 1993; Marsh et
72 al., 1997; Vasconcelos et al., 1994), western Africa (Vasconcelos et al., 1994), and
73 Australia (Bird et al., 1990; Vasconcelos et al., 2003). However, direct dating of
74 weathering and supergene mineralization in Central Asia by K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ of the
75 supergene K-bearing sulfates is rare. Only Xu et al. (2008), He et al. (2009), and
76 Chen et al. (2014) reported the K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ results for jarosite or other
77 supergene K-bearing minerals (ferricopiapite, voltaite, yavapaiite) from the oxidation
78 zone of the Hongshan (K-Ar ages) and Baiyin deposits ($^{40}\text{Ar}/^{39}\text{Ar}$ ages, Gansu
79 Province).

80 The Tulufan-Hami (Tu-Ha) Basin is one of the major hyperarid regions in
81 northwestern China. This basin is surrounded by two large Asian mountain ranges: the
82 Tibetan Plateau to the south and the Tianshan range to the north and northwest.
83 Compared with extensive studies on the other arid basins (e.g., Tarim, Junggar) in
84 Northwest China (Sun et al., 2006, 2008, 2009, 2013, 2015; Tang et al., 2011; Zhang
85 et al., 2011), less is known about the history of the aridity and the associated forcing

mechanisms of aridification in the Tu-Ha Basin. Only one study of multiple climatic proxy parameters from the discontinuous sequence of the Lianmuqin section in the Tu-Ha Basin indicates a record of Cenozoic climatic change (Cheng, 2005). Deep weathering profiles and associated supergene oxidation zones are widely distributed throughout the Tu-Ha Basin (Tu et al., 1963; Fang et al., 2002; Xu et al., 2006, 2008; Qin et al., 2001, 2008; He et al., 2009), in which alunite group minerals, especially jarosite, are commonly found. Their abundance in weathering profiles and their ease of access for complete sampling at deposit sites provide an excellent opportunity to date weathering processes and the formation of the oxidation zone of sulfide deposits by the $^{40}\text{Ar}/^{39}\text{Ar}$ method. In this paper, we address the reliable and promising dating method — $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology—to study three weathering profiles (the Hongshan deposit, the Liuhuangshan deposit, and the Caihuagou deposit) to place precise constraints on the timing and duration of weathering and supergene enrichment in the Tu-Ha basin. Based on these results and previously published data (Xu et al., 2008; He et al., 2009; Yang, 2013), we infer the paleoclimatic conditions that led to the formation of the oxidation zone of these sulfide deposits and discuss the forcing mechanisms controlling the regional aridification of the Tu-Ha Basin.

2 Geological setting

The Tu-Ha Basin, located in the north of the Tibetan Plateau, is surrounded by the Tian Shan Mountains to the north and northwest (Fig. 1). The basin is currently characterized by a hyperarid climate, with a mean annual temperature of 14 °C, a mean annual rainfall of approximately 28 mm (Tulufan~17 mm/yr; Hami~34 mm/yr),

and mean annual evaporation over 3000 mm, which makes it one of the driest deserts in the Asian interior (Fig. 2a, b) (Li et al. 1993; Miao et al., 2012). Large areas of the Tu-Ha Basin are mantled by thick supergene oxidation zones, which developed over sulfide ore deposits and host the most common supergene sulfate minerals: jarosite, alunite, and yavapaiite (Fig. 2) (Tu et al., 1963; Fang et al., 2002; Xu et al., 2006, 2008; Qin et al., 2001, 2008; He et al., 2009). In this paper, we focus on studying three sulfide deposits: the Hongshan deposit, the Liuhuangshan deposit, and the Caihuagou deposit (Fig. 1).

The Hongshan deposit (E91°28'-92°00', N42°34'-42°40') is a large high-sulfur hydrothermal Cu-Au deposit, which is situated in the center of the Tu-Ha Basin (Qin et al., 2001; Fang et al., 2002) (Fig. 1). The elevation of this deposit is 450-500 m above sea level, and the landscape is dominated by very gentle topographic relief (Fig. 2a). The southern part of this deposit is composed of quartz diorite-monzonitic granite-biotite granite, whereas the north is composed of Silurian-Devonian basic volcanic rocks. The central portion of this deposit, related to copper and gold mineralization, comprises Mesozoic intermediate-acidic volcanic rocks that are mainly composed of quartz porphyry, albite porphyry, dacite, dacite porphyry, andesitic porphyrite, and dioritic porphyrite (Qin et al., 2001; Fang et al., 2002; Xu et al., 2008). Ore minerals include pyrite, chalcopyrite, bornite, chalcocite, and natural gold (Fang et al., 2002). The supergene enrichment forms a 50-60 m deep weathering profile, which provides suitable phases for weathering geochronology (Qin et al., 2001, 2008; Xu et al., 2006, 2008). Supergene jarosite mainly occurs at the bottom of

the iron cap (0.5 m to 2 m below the surface) as a yellow subhorizon (Fig. 2c). A new supergene K-bearing sulfate mineral (yavapaiite) occurs at 14-15 m below the surface and is also found in the oxidation zone of this sulfide deposit.

The Liuhuangshan deposit (E88°28'20", N41°58'00") is located along the southwestern margin of the Tu-Ha Basin (Fig. 1). The elevation of this deposit is approximately 1050-1200 m above sea level. The ore deposit was discovered in the Hercynian quartz porphyry rock body, which is intruded into the Upper Ordovician Liuhuangshan sedimentary stratum (Li, et al., 2003). The wall rock alteration near the ore body is very strong, and it mainly presents as silication, pyritization, sericitization, and baratization (Li, et al., 2003). The primary ores are pyrite, chalcopyrite, cupriferous pyrite, sphalerite, and chalcocite (Li, et al., 2003). In this deposit, intense weathering has produced thick weathered profiles, up to 30 m thick (Fig. 2d). Supergene jarosite mainly occurs at the bottom of the iron cap as a yellow sub-horizon whose thickness can be up to 8 m.

The Caihuagou deposit (E88°53'00"-88°56'40", N42°08'20"-42°09'56") is located approximately 20 km northeast of the Liuhuangshan deposit (Fig. 1). The elevation of this deposit is 1100-1280 m above sea level. The ore deposit is hosted by the lower Devonian Arpishmebulaq Formation of the central Asia group, in which rocks have different degrees of deformation and metamorphism because of regional metamorphism (Si et al., 2011). The main rocks here are chlorite quartz schist, sericite quartz schist sandwiched marble, and biotite quartz schist. Primary ores are mainly pyrite, chalcopyrite, and sphalerite, as well as small amounts of molybdenite, and

tetrahedrite (Si et al., 2011). An oxidation zone has formed at the top of the deposit, and it mainly includes jarosite, limonite, covellite, and malachite. Supergene jarosite mainly occurs at the bottom of the iron cap and is distributed at 0.5 m to 3 m below the surface (Fig. 2e).

3 Sampling and analytical procedures

Supergene K-bearing sulfates suitable for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology were collected from the three weathering profiles. During the course of sampling, we collected jarosite samples exhibiting cavity infillings (Fig. 2f, g), which are generally devoid of contaminants and thus ideal for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. At Hongshan, samples were collected from discrete mining pits that span approximately 20 m depth: supergene jarosite samples collected from 0.5 m to 2 m below the surface and yavapaiite samples collected from 15 m below the surface (pale pink mineral, Fig. 2h). At the Liuhuangshan deposit, the jarosite samples were obtained from 4 m to 5 m below the surface (although systematic sampling from the top to the bottom was permitted, the remaining collected samples had not been dated). At the Caihuagou deposit, jarosite samples were obtained only at the bottom of the iron cap on the hilltops, and collection of additional samples at depth was not possible due to inaccessibility. We investigated eleven supergene K-bearing mineral samples in the three weathering deposits.

Polished thin sections of each sample were studied by transmitted- and reflected-light microscopy to determine the mineralogy and paragenesis of the sample. In addition, optical microscopy was used to determine whether this sample contains

primary minerals (i.e., quartz, feldspar). After petrographic examination, suitable samples were crushed, washed in acetone in an ultrasonic bath, and dried. For each sample, 1-2 g of grains (approximately 60-100 mesh) were handpicked under a binocular microscope. The purity, composition, and crystallinity of these samples were further investigated by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) (Vasconcelos, 1994, 1999a, 1999b).

The X-ray powder diffraction analysis was conducted at the Beijing Micro-structure Analytical Lab. Approximately 30 mg of powders were analyzed in a Dmax 12 kW diffractometer equipped with a Cu X-ray tube operating at 40 kV and 100 mA, with a 2-65° scan range and a scan speed of 8 °(2θ)/min.

Three to five grains were mounted in an epoxy container and polished for scanning electron microscopy (SEM) at the Institute of Geology, Chinese Academy of Geological Science, National Key Laboratory of Continental Structure and Dynamics. The mounted grains were carbon coated and then observed in the secondary electron and backscattered electron modes. Simultaneously, the equipped energy dispersive spectrometer was used to analyze the morphology and composition.

On the basis of the XRD and SEM-EDS investigations, 10 mg to 30 mg of mineral grains from each sample were wrapped in aluminum foil, sealed in a silica glass tube with ZBH-25 biotite standards, and irradiated for approximately 5-14 hours at the China Institute of Atomic Energy. After a 3 month cooling period, the samples were analyzed by the incremental heating $^{40}\text{Ar}/^{39}\text{Ar}$ method. To test the reproducibility of the experimental results, two aliquots of two samples (HS-20 and

HS-52) were tested. One grain (HS-20-1) of sample HS-20 and the yavapaiite sample (K101) were analyzed at the State Key Laboratory of Earthquake Dynamics, Institute of Geology, China Earthquake Administration. The aliquots were heated using a double-vacuum resistance furnace, whose stability of temperature control and temperature accuracy is better than ± 5 °C. The fraction of gas released in an ultra-high vacuum system was cleaned with a cold-trap (-80 to -100 °C), titanium sponge, and two Zr-Al getters operated at ~ 400 °C and at room temperature, and then analyzed for Ar isotopes in a mass spectrometer. The remaining jarosite samples were analyzed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, China Academy of Sciences. Each sample was transferred to a 30-pit copper disk and incrementally heated under a continuous laser (COHERENT-50 W CO₂ laser) with a 2 mm-diameter beam. Argon gases were extracted for 60-70 s at each designated power, the fraction of gas released was cleaned through a cryocooled cold-trap (-130 °C), and two SAES NP10 Zr-Al getters operated at ~ 400 °C and at room temperature. Then, the cleaned gases were admitted into a VG5400 mass spectrometer. All data were corrected for mass discrimination, radioactive decay and nucleogenic interferences. The $^{40}\text{Ar}/^{39}\text{Ar}$ dating results (except yavapaiite samples: K101-1 and K101-2, which were calculated and plotted using the software from the $^{40}\text{Ar}/^{39}\text{Ar}$ laboratory at the State Key Laboratory of Earthquake Dynamics) were calculated and plotted using the ArArCALC software version 2.5.2 (Koppers, 2002).

4 Results

4.1 Petrographical and Mineralogical patterns

Petrographic observations and XRD analysis indicate that most of the jarosite samples are primarily composed of jarosite, with minor amounts of tamarugite, sideronatrite, and quartz. Small amounts of quartz (<3%) were found in two samples (CHG2-5, CHG2-8), which were checked and selected repeatedly to eliminate the influence of the contaminants as much as possible. However, quartz was not found in the SEM analysis. Furthermore, the influence of quartz is not reflected in the subsequent age spectra. One jarosite sample consists of fine-grained powdery yellow jarosite clusters (HS-20, <5 μm , Fig. 3a, b, c). The other samples consist of coarse-grained orange-brown euhedral jarosite (Fig. 3d, e, f; Fig. 4). The SEM image and the XRD patterns show that the coarse-grained jarosites are well-crystallized and exhibit three different crystal habits: pseudocubic morphologies (LHS-5), hexagonal pyramid morphologies (LHS-1, LHS-2), and tabular morphologies (HS-52, CHG2-4, CHG2-5, CHG2-8, LHS-3, LHS-4). The XRD and SEM analyses indicate some isomorphic substitution of Na or H_3O^+ for K in the A site of the jarosite structure (Fig. 3c, f; Fig. 4d). Additionally, the results of the analysis of the LHS-5 sample indicate substitution of Pb and Al for Fe in the B site and substitution of PO_4^{3-} in the SO_4^{2-} site of the jarosite structure (Fig. 4d).

In this study, one new weathering mineral, yavapaiite ($\text{KFe}(\text{SO}_4)_2$), which has high potassium content (13.6%), is identified as being a potential mineral for dating weathering processes using $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. Yavapaiite minerals are directly precipitated from weathering solutions, and are intergrown with dark green

ferronatrite and olive green voltaite. Yavapaiite is characteristically fibrous, radial in aggregates, and pale pink (Fig. 5a). The XRD and SEM analyses indicate that the sample K101 is composed of yavapaiite (Fig. 5b, c).

4.2 $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology

A total of 15 grains from 11 supergene K-bearing sulfate hand samples were analyzed by the $^{40}\text{Ar}/^{39}\text{Ar}$ method. All results, corrected for interfering isotopes and mass discrimination, are listed in an Appendix as Supplementary data. A summary of these results is listed in Table 1. In this study, an age plateau is defined as a sequence of three or more continuous steps that contain more than 50% of the total amount of ^{39}Ar released, and they yield apparent ages reproducible at the 95% confidence level. Uncertainties on all of the results are reported at the 1σ level.

4.2.1 Hongshan deposit

In the Hongshan deposit, seven grains from three samples yield very well-defined ages ranging from 8.1 ± 0.3 Ma to 3.3 ± 0.4 Ma. The analysis results of two visually distinct jarosite samples are shown in Fig. 6. One jarosite sample (HS-20) exhibits very fine-grained powdery yellow clusters. The other sample (HS-52) is coarse-grained with yellow-brown euhedral crystals. For each of the grains of the fine-grained jarosite sample HS-20 (HS-20-1, HS-20-2, HS-20-3; Fig. 6a, b, c), the isochron age is consistent with the plateau age, and the $^{40}\text{Ar}/^{36}\text{Ar}$ intercept is close to the atmospheric ratio (295.5) (even though the three grains were analyzed by two laboratories), indicating that there is no excess argon in the sample. The ^{39}Ar recoil effect of the samples is not appreciable. The three different grains all yield ages of

approximately 7.8 Ma and are indistinguishable within errors. These results are similar to those for the coarse-grained jarosite sample HS-52 (HS-52-1, HS-52-2; Fig. 6d, e). The isochron age is consistent with the plateau age for each grain and the ages for the two different grains are indistinguishable within errors at 8.1 Ma. The spectra of grain HS-52-1 indicates a minor ^{39}Ar loss by recoil, but had a negligible effect on the age (Fig. 6d). The spectra of the above samples suggest that contamination of old phases did not occur in these samples. The consistency of results between the two samples demonstrates that the grains represent a single generation, their ages are true precipitation ages of the jarosites analyzed, and both fine-grained and coarse-grained jarosites are suitable for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology.

Theoretically, any supergene mineral that contains K in a crystallographic site is potentially suitable for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, provided that the mineral retains K and Ar quantitatively (Vasconcelos, 1999b). Thus, we also analyzed yavapaiite using the $^{40}\text{Ar}/^{39}\text{Ar}$ method. Fig. 6 (f, g) shows the step-heating spectra and inverse isochron plots of yavapaiite sample K101. For the grains K101-1 and K101-2, the isochron age is consistent with the plateau age within errors, and the $^{40}\text{Ar}/^{36}\text{Ar}$ intercept is close to the atmospheric ratio (295.5). The spectra of K101-1 and K101-2 may show that a minor amount of ^{39}Ar is lost by recoil, but a meaningful plateau age is also retrieved (Fig. 6f, g). Although there is a slight difference in the ages between grains K101-1 and K101-2, we suggest that this difference is acceptable within errors.

4.2.2 The Liuhuangshan and Caihuagou deposits

In the Liuhuangshan and Caihuagou deposits, eight samples yield well-defined

ages, ranging from 33.3 ± 0.5 Ma to 8.9 ± 0.2 Ma (Fig. 6h-o). Despite the fact that only one grain from each sample was analyzed, the consistency between the plateau age and the isochron age for each sample and the proximity of the $^{40}\text{Ar}/^{36}\text{Ar}$ intercept to that of the atmospheric ratio, suggest that the samples did not undergo argon loss after their formation and contained no excess argon. Moreover, characteristics of the spectra suggest that ^{39}Ar loss by recoil occurred in some samples. Age spectra of the five Lihuangshan and Caihuagou samples (LHS-1, LHS-2, LHS-3, LHS-4, CHG2-5; Fig. 6h-k, n) display an initial 3-5 steps with anomalously high apparent ages, followed by a series of high-temperature steps defining a plateau. These spectra reflect the loss of a small amount of recoiled ^{39}Ar to the surrounding atmosphere during the irradiation or bake-out procedure because the crystal domains of these samples are <5 to $10\ \mu\text{m}$ (Vasconcelos, 1999a). The initial 3-4 steps in these spectra contain mostly atmospheric ^{40}Ar and ^{36}Ar because of a large amount of atmospheric argon is trapped in the intercrystalline sites of the jarosite samples. Small amounts of radiogenic $^{40}\text{Ar}^*$ released during the initial 3-4 steps are derived from sites that have lost ^{39}Ar by recoil. In these cases, the plateau age represents the true precipitation age, whereas the integrated age is older than the plateau age. The spectra from sample LHS-5 (Fig. 6l) shows anomalously low apparent ages in the low-temperature steps, anomalously high apparent ages in subsequent steps, and a sequence of high-temperature steps defining a plateau. This spectra indicates that recoiled ^{39}Ar has been reimplanted or trapped within less retentive sites in the jarosite mineral (Vasconcelos, 1999a). The initial steps, although containing mostly atmospheric Ar,

also contain radiogenic $^{40}\text{Ar}^*$ and $^{39}\text{Ar}_{\text{recoiled}}$ easily released from their implantation or trapping sites. In this case, the integrated age is lower than the plateau age. For the all of the above samples, ^{39}Ar recoil loss is not significant. These samples still yield well-defined plateau ages, suggesting that the ^{39}Ar recoil had only a minor or negligible effect on these samples and the results provide reliable constraints on the formation ages of the supergene jarosites.

5 Discussion

5.1 Cenozoic weathering of the Tu-Ha Basin

The ages of eleven supergene K-bearing sulfate samples (jarosite, yavapaiite) from the three weathering profiles in the Tu-Ha Basin have been combined with published data on the K-Ar ages (one ferricopiapite is 8.6 Ma; one yavapaiite is 4.1 Ma; two voltaites are 14.7 Ma and 8.6 Ma; one jarosite is 11 Ma) (Xu et al., 2008; He et al., 2009; Yang, 2013). They range from 33.3 ± 0.1 Ma to 3.3 ± 0.4 Ma (1σ) (Fig. 7), indicating a protracted history of weathering and supergene enrichment from the beginning of the Oligocene to the middle Pliocene. The five jarosite samples from the Liuhuangshan deposit yield well-defined $^{40}\text{Ar}/^{39}\text{Ar}$ ages ranging from 33.3 Ma to 14.8 Ma, hosting the relatively old weathering event from the Oligocene to the middle Miocene. The Caihuagou profile, located approximately 20 km northeast of the Liuhuangshan deposit, yielded $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages in a range of 27.3 to 8.9 Ma, revealing late Oligocene to late Miocene weathering and supergene enrichment. The two closely spaced deposits show similar weathering histories. However, ages younger than 8.9 Ma are absent. This does not mean that weathering ceased for the

two deposits because the younger samples, which are often present at great depth, were not dated (Liuhuangshan profile) or were not available during the course of sampling (Caihuagou profile). The Hongshan profile yielded $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages between 14.7 and 3.3 Ma, indicating a history of weathering and supergene enrichment from the middle Miocene to the middle Pliocene. The youngest results (4.1-3.3 Ma) correspond to yavapaiite samples collected at 14-15 m below the surface (Fig. 2c), and represent the most recent weathering in the profile. Likewise, the absence of older geochronological results does not preclude a much older weathering history for this deposit. Older supergene minerals may have been removed from the upper parts of the profile by erosion, or they may have been dissolved or undergone subsequent dissolution - reprecipitation reactions. Therefore, taken together, the present geochronological results of weathering minerals may provide a minimum constraint on the timing and the duration of the weathering process, indicating that weathering may have operated since at least the Oligocene (Fig. 7).

Weathering processes and supergene enrichment are ultimately controlled by five major factors: the nature of the bedrock, climate, tectonism, biological activity, and time, in which climate and tectonics are frequently considered as the major regional controls (Thomas, 1994; Vasconcelos, 1999a; Deepthy et al., 2005; Borrelli et al., 2012, 2014; Perri et al., 2012, 2014, 2015). The dating of supergene sulfate minerals from different profiles at a regional scale should yield internally consistent results. However, the ages from the Liuhuangshan profile and the Caihuagou profile are clearly older than those from the Hongshan profile. We suggest that such an age

discrepancy among weathering ages may be attributed to differences in the elevations of the three deposits. According to the “uplift-scarp retreat” landscape model, the ages of the weathering profiles should increase from the lowest to the highest elevation. The elevations of the Liuhuangshan deposit and the Caihuagou deposits are approximately 1100 m above sea level, and the topographic relief of those areas is higher than that of the Hongshan deposit, which is located at 450-500 m above sea level (Fig. 2). Despite the discussion above, the ages of the Liuhuangshan and Caihuagou profiles still partially overlap with those from the Hongshan profile. In addition, the three deposits are located in relatively stable tectonic areas (Deng et al., 2000). As noted by Vasconcelos (1999b), since the start of weathering, continental areas hosting ancient weathering profiles must not be located in tectonically active areas where erosion rates are high because the weathering profiles would not be preserved. Therefore, the present geochronological data indicate that the age of weathering in the three deposits, although not identical, are temporally consistent, and they suggest that the evolution of weathering profiles is mainly dependent on regional climate.

A current controversy is whether the evolution of weathering profiles is continuous or episodic through time. The continuous model of weathering suggests that the parent rocks are continuously exposed to air and water; thus, weathering reactions proceeded constantly. However, the episodic model argues that weathering reactions are chemical reactions and therefore can be intense under favorable conditions. Our weathering age results seem to support the hypothesis that weathering

reactions and the associated formation of supergene sulfate minerals **have** occurred with variable intensity since the Oligocene, and this may reflect an episodic distribution of **the weathering ages**. Due to the limited number of samples collected in this paper, this conclusion cannot yet be confirmed. To address this issue further, a much larger number of samples at different sites must be dated, and sampling of the whole weathering profile is necessary.

5.2 Implication for the arid paleoclimate

Deep chemical weathering and associated supergene enrichment are favored under arid-semiarid climate conditions, which provide sufficient groundwater for the precipitation of jarosite and other weathering minerals under appropriate redox conditions. Once the minerals precipitate, the preservation of these minerals requires a transition toward increased aridity with a resulting drop in the water table. Otherwise, the supergene K-bearing sulfate minerals may be unstable when exposed to a saline environment (pH>3.5). Therefore, massive formation of supergene K-bearing sulfate minerals in sulfide ore deposits and other weathering profiles is a good indicator of arid-semiarid paleoclimatic conditions and a transition toward hyperaridity (Alpers et al., 1988; Vasconcelos et al., 1994; 1999a). A typical application of weathering geochronology is the aridification history of the Atacama Desert. K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of supergene alunite and jarosite from several porphyry copper deposits show that a prevalence of regionally arid-semiarid conditions existed throughout the late Oligocene to **the** middle Miocene, with a late transition to hyperaridity in the Atacama region (Araibia et al., 2006). Therefore, although the age results of the three profiles

presented here is rather limited for a comprehensive study of the Tu-Ha Basin, we use the distribution of supergene ages obtained from previously published results (Hongshan deposit) (Xu et al., 2008; He et al., 2009; Yang, 2013) and this study to reflect the aridification history of the Tu-Ha Basin (Fig. 7).

From the ages of the supergene sulfate minerals, the earlier jarosite age (33.3 ± 0.5 Ma) appeared at the Eocene/Oligocene boundary, and four ages appeared in the late Oligocene. We suggest that the arid-semiarid climate over the basin may have emerged at the beginning of the Oligocene and the late Oligocene. This consideration is consistent with the sedimentary records in the Tu-Ha Basin (Cheng, 2005). In the Tu-Ha Basin, a nearly sedimentary records (Lianmuqin section) provides abundant information on the Cenozoic climate in this basin (Cheng, 2005) based on multiple climatic proxy parameters. During the Oligocene, the geochemistry of the sedimentary rocks in the Lianmuqin section in the Tu-Ha Basin (Cheng, 2005) show high $\text{FeO}/\text{Fe}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$, high CaCO_3 content (the average value is 15.01%, which is higher than all of the other Cenozoic values except for those in the Pliocene), and clearly negative organic carbon isotope values, which document an arid-semiarid climate (Cheng, 2005). Additionally, common fossil plants found in the section are *Ephedripites*, *Nitrariadites*, and *Labitricolpites*, which favor conditions of arid-semiarid climate (Yang et al., 1994). Fossil evidence of the large mammals *Paraceratherium lipidus*, *Dzungariotherium turfanensis*, and *Cadurcodon ardynense*, which are tolerant of arid climates, is also found in the Tu-Ha Basin (Li, 1983). These lines of evidence strongly suggest that the climate at the beginning of the Oligocene

and the late Oligocene was arid-semiarid. However, because of the limited amount of data, our results cannot document whether the arid-semiarid climate lasted for the entire early Oligocene.

Between 23.3 and 16.4 Ma, no significant ages are recorded by the supergene K-bearing sulfate minerals in the three profiles. The absence of this age range does not mean that drier conditions prevailed regionally during all of this period because only three deposits were dated for the whole Tu-Ha Basin. Yet another important reason may be that the analysis of the Lianmuqin section in the early Miocene (before 15 Ma) shows that the rocks (1) are characterized by brick-red and brownish-red colors, (2) contain high values of SiO₂ (the highest value is 72.9%, and average value is 63.05%) and Fe₂O₃/(Fe₂O₃+FeO), and (3) exhibit a much lower CaCO₃ content (average value is 4.73%) (Cheng, 2005), all of which suggest that the climate was relatively warm and wet in the early Miocene. These conditions could have led to the dissolution jarosite, or to rapid erosion rates that may have precluded the preservation of the supergene jarosite. How, then, can the Oligocene jarosite be preserved after this warm and wet climate period? The answer is possibly related to the preferential migration of oxygenated surface water along a permeable horizon or along fracture planes that may allow the preservation of older weathering minerals formed earlier at lower levels in the profile, even if the jarosite in the upper layer was eroded or dissolved. Compared with the major element geochemical results from the sediments in the Lianmuqin section of the early Miocene, the middle Miocene (15-11 Ma) results have lower SiO₂, Al₂O₃, Fe₂O₃, and Fe³⁺/Fe²⁺, but a slightly higher FeO and

438 substantially higher CaCO_3 and organic carbon concentrations. In addition, columnar
439 gypsum is present in this formation, which may indicate that the temperature of this
440 period decreased and that climate shifted toward more arid conditions. Since 11 Ma,
441 the contents of Al_2O_3 , Fe_2O_3 and FeO slightly increased, and the $\text{SiO}_2/(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3)$
442 slightly decreased, which may demonstrate that, overall, the temperature increased
443 slightly during this period. Furthermore, there are several crystalline gypsum layers
444 that exhibit thicknesses up to 1-2 m, thereby suggesting a relatively arid-semiarid
445 climate (Cheng, 2005). In the Miocene, $^{40}\text{Ar}/^{39}\text{Ar}$ ages ranging from 16.4 Ma to 14.7
446 Ma may confirm that the semiarid-arid climate started to reappear, followed by a
447 period from 11 to 7.8 Ma in which regionally arid-semiarid conditions prevailed, with
448 at least a moderate amount of precipitation (>10 cm/y, Clark et al., 1990). Afterward,
449 a drop in the water table caused by a transition toward hyperarid conditions allowed
450 for the preservation of the jarosite minerals. The two ages of yavapaiite samples,
451 which yielded the youngest results (4.1 Ma and 3.3 Ma), were collected at 14-15 m
452 below the surface in the Hongshan profile. We suggest that the age vs. depth trend
453 observed in the Hongshan profile (Fig. 8) records a drop in the water table, and
454 therefore increasingly arid climate conditions. In summary, after 11-7.8 Ma, a
455 continuous drop in the water table to 14-15 m below the present ground surface
456 allowed for the formation of yavapaiite minerals, and then the water table dropped
457 again to preserve these minerals. Notwithstanding the potential sampling issues
458 mentioned earlier, the lack of exposure of the younger ages after 3.3 Ma in this study
459 may be in response to the cessation of supergene oxidation by that time due to the

hyperarid conditions. The CaCO_3 content of the Lianmuqin section in the Pliocene reflects a dramatic increase up to the highest value (39.1%) between 4.5-4 Ma, with relatively high values (more than 30%) lasting until the late Pliocene (Cheng, 2005). The increase in CaCO_3 content, as well as much higher CaCO_3 contents overall, indicate that the climate became hyperarid (Cheng, 2005). A thick (1-2 m) gypsum bed, also found in the Pliocene series near the Lianmuqin section in the northwest Tu-Ha Basin, provides additional evidence for the hyperarid climate. This may suggest that extreme aridity prevailed in the Tu-Ha Basin when (or after) the yavapaiite precipitated.

5.3 Factors controlling the arid paleoclimate

Our evidence demonstrates that an arid-semiarid climate may have emerged at the beginning of the Oligocene and in the late Oligocene, with regionally pervasive arid-semiarid conditions during the late Miocene followed by a transition toward hyperarid conditions. It is interesting to discuss potential causes of the aridification of the Tu-Ha Basin.

In recent years, an increasing amount of research suggests that the retreat of the Cenozoic Paratethys Sea provides the key factor for the aridification of Central Asia (Ramstein et al., 1997; Zhang et al., 2007; Bosboom et al., 2013; Sun et al., 2010, 2013). The Tethys closed during the collision of the Indian continent with Asia. Subsequently, the isolated Paratethys Sea formed around the beginning of the early Oligocene due to climatic cooling induced by a drop in eustatic sea level and/or tectonic uplift of the Pamir Mountains, the West Kunlun Shan, and the Tian Shan

(Rögl et al., 1999; Schulz et al., 2005). Ramstein et al. (1997) noted that the Paratethys Sea, which extended across Eurasia, was the main source of moisture for northwest China, and its retreat would notably increase the aridity in that region in the early Oligocene. Detailed experiments carried out by Zhang et al., 2007 confirmed that the retreat of the Paratethys Sea strengthened the summer monsoon and greatly increased the humidity in the monsoon-affected areas and the overall aridity of northwest China. Furthermore, they found the westward retreat of the Paratethys Sea to the Turan Plate in the Oligocene to be the key control for the pattern of paleoenvironmental transitions in northwestern China. Thus the most pronounced effect of the retreat of the Paratethys Sea on the Asian climate occurred during the Oligocene. The five ages obtained in our results suggest that the arid-semiarid climate may have emerged in the Oligocene, concomitant with the retreat of the Paratethys Sea, which would reduce westward water vapor transport by the westerlies to the Tu-Ha Basin and lead to its aridification.

The supergene K-bearing sulfate mineral $^{40}\text{Ar}/^{39}\text{Ar}$ ages (16.4-7.8 Ma) presented here identify the timing of the initiation for the transition to semiarid-arid conditions in the middle Miocene and a period of prevailing arid-semiarid climate conditions at 11-7.8 Ma. After 7.8 Ma, we suggest that the climate shifted toward hyperarid conditions. What mechanism brings about such a transition to hyperaridity? The Tu-Ha Basin is located in the rain shadow of the Tibetan Plateau, and its north and northwestern edges are defined by the Tianshan Mountains. Thus, the regional tectonic effects related to active mountain building may be the major influencing

504 factors. [Harrison et al. \(1992\)](#) and [Molnar et al. \(1993\)](#) summarized the tectonic
505 events in the areas surrounding Tibet and suggested that a rise of Tibet reached its
506 highest elevation near 8 Ma. Recent studies show that significant crustal shorting and
507 tectonic uplifts along the northern edge of the Tibetan Plateau occurred [ca. 15-8 Ma](#)
508 [\(Lease et al., 2007; Ritts et al., 2008; Bovet et al., 2009; Zheng et al., 2010; Lease et](#)
509 [al., 2011\)](#), which could act as a barrier to the flow of the humid Indian monsoon
510 passing through the Himalaya range and lead to the intensified aridity in the Tu-Ha
511 Basin. Additionally, [because the Tu-Ha Basin is bounded by the Tianshan range to the](#)
512 [north and northwest, we suggest that the uplift of the Tian Shan Mountains may also](#)
513 [be a factor partially affecting the hyperaridity in the Tu-Ha Basin. Zhang et al. \(2011\)](#)
514 [and Sun et al. \(2015\) presented evidence that shows that the uplift of the Tianshan](#)
515 [range played an important role in controlling the aridification that commenced since](#)
516 [the latest Miocene in the Tarim Basin.](#) In fact, the amount of rainfall in the northern
517 and northwestern Tian Shan piedmont today is one order of magnitude greater
518 (162-264 mm/y) than in the Tu-Ha Basin. Numerous studies document the tectonic
519 uplift of the Tian Shan region based on thermochronology, sediment research, and
520 paleobotanical analysis. In early studies, magnetostratigraphic sections and fission
521 track ages in the eastern and southern Tian Shan indicated that erosional exhumation
522 of these ranges began at 20-25 Ma ([Hendrix et al., 1994; Sobel et al., 1997; Yin et al.,](#)
523 [1998](#)). However, the extrapolation of geodetic shortening rate suggested that the
524 initial growth of the Tian Shan occurred at ~10 Ma ([Avouac et al., 1993;](#)
525 [Abdrakhmatov et al., 1996](#)). [Bullen et al. \(2001, 2003\)](#) applied paired bedrock

fission-track and U-Th/He ages from the northwestern Tian Shan to demonstrate that rapid exhumation commenced at ca. 11 Ma. Sun et al. (2004) applied detailed magnetostratigraphic studies of the molasse deposits of the folded Neogene and Quaternary strata on the northern edge of the Tian Shan, which indicated that the onset of uplift occurred at ~7 Ma. In a relatively wide area of the Tian Shan Range, the Kuitun He section shows evidence of active uplift at ~10.5 Ma (Charreau et al., 2005). Zhang et al. (2011) presented evidence from the Kuchetawu section and clearly showed that the uplift of the southern Tian Shan Range occurred at ~7 Ma. Zhu et al., (2006) analyzed apatite and zircon samples by fission-track thermochronology from the Bogda-Harlik Mountains, and the thermal history model showed that exhumation occurred in the late Cenozoic (12-7 Ma). Although there are inconsistencies among the above results, most of them demonstrate that the uplift of the Tian Shan occurred in the late Miocene. Uplift of the Tian Shan along with that of the Tibetan Plateau resulted in the conversion of the Tu-Ha Basin into an intermontane basin. In addition, reduced eastward water vapor transport via the westerlies due to orographic blocking may also enhance aridity. Therefore, both the uplift of the Tibetan Plateau and the Tian Shan during the middle-late Miocene played important roles in the aridification history of the Tu-Ha Basin since the late Miocene. The increasing rain shadow effect of the uplifted mountains likely resulted in increased aridity, which resulted in a continually falling water table, such that the yavapaiite minerals at 14-15 m below the surface in the Hongshan profile were preserved.

6 Conclusions

The application of $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology to supergene K-bearing sulfate minerals collected from three weathering profiles in the Tu-Ha Basin, yields well-defined ages ranging from 33.3 ± 0.5 Ma to 3.3 ± 0.4 Ma (1σ). When combined with previously published ages, our data indicate a protracted history of weathering processes and supergene enrichment from the Oligocene to the middle Pliocene. This suggests that an arid-semiarid climate with at least a moderate amount of precipitation (>10 cm/y) probably emerged in the Tu-Ha Basin at 33.3 Ma, 27.7-23.3 Ma, 16.4-14.7 Ma, and regionally prevailed from 11-7.8 Ma. Afterward, a progressive change occurred from arid-semiarid towards hyperarid climatic conditions. Predominantly hyperarid conditions may have persisted since at least ca. 3.3 Ma. The climatic implications inferred from the weathering geochronology are in agreement with the major element and isotope compositions of the Cenozoic sediments from the Lianmuqin section in the Tu-Ha Basin, attesting to the reliability of weathering geochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ method as an indicator of paleoclimate in arid areas. The $^{40}\text{Ar}/^{39}\text{Ar}$ results also lead us to propose that regional aridification in the Oligocene was a response to the retreat of the Paratethys Sea and that the aridification history of the Tu-Ha Basin since the late Miocene was mainly controlled by regional tectonic uplift.

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Figure 1

Figure 2

Figure 3

Figure 4

Element	a	b	c
Na	1.32	2.26	2.61
S	14.48	14.84	15.59
K	5.81	6.31	6.71
Fe	31.27	40.67	38.45
O	36.36	35.93	36.64
Al	1.67		
P	1.55		
Pb	7.53		

Figure 5

Figure 6

Figure 7

Figure 8

Table 1

Table1 Summary of the ⁴⁰ Ar/ ³⁹ Ar ages of supergene K-bearing sulfate minerals from Tu-Ha Basin						
Sample	Grain	Plateau Age (Ma)	Isochron Age (Ma)	Intercept ⁴⁰ Ar/ ³⁶ Ar	Integrated Age (Ma)	Comments
Hongshan profile						
HS-20	HS-20-1	7.8±0.2	7.6±0.3	296.8±1.2	10.4±0.9	Plateau
	HS-20-2	7.8±0.5	7.6±1.5	295.7±2.8	7.8±0.6	Plateau
	HS-20-3	7.7±0.2	7.8±0.7	295.2±1.5	7.9±0.3	Plateau
HS-52	HS-52-1	8.1±0.2	8.1±2.0	295.4±5.0	8.4±0.3	Plateau
	HS-52-2	8.1±0.2	8.2±1.4	295.3±4.0	8.1±0.2	Plateau
K101	K101-1	3.3±0.4	3.0±0.7	298.6±6.4	4.3±1.4	Minor ³⁹ Ar recoil, Plateau
	K101-2	3.9±0.6	3.4±5.4	299.0±41	4.8±1.5	Minor ³⁹ Ar recoil, Isochron
Liuhuangshan profile						
LHS-1	LHS-1-1	23.3±0.4	23.4±1.7	295.5±0.9	36.5±0.8	Minor ³⁹ Ar recoil, Plateau
LHS-2	LHS-2-1	27.7±0.4	27.9±1.6	295.4±0.6	79.5±0.9	Minor ³⁹ Ar recoil, Plateau
LHS-3	LHS-3-1	14.8±0.3	14.3±1.2	295.7±0.5	53.4±0.7	Minor ³⁹ Ar recoil, Plateau
LHS-4	LHS-4-1	33.3±0.5	33.1±1.5	295.6±0.5	55.0±0.8	Minor ³⁹ Ar recoil, Plateau
LHS-5	LHS-5-1	26.1±0.1	26.7±0.5	289.4±4.5	25.8±0.2	Minor ³⁹ Ar recoil, Plateau
Caihuagou profile						
CHG2-4	C2-4-1	8.9±0.2	8.8±0.4	296.0±0.7	12.7±0.6	Plateau
CHG2-5	C2-5-1	16.4±0.4	16.4±0.9	295.4±0.9	23.0±0.9	Minor ³⁹ Ar recoil, Plateau

CHG2-8	C2-8-1	27.3±0.6	27.3±2.0	295.5±1.2	27.5±0.7	Plateau
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Figure Captions

Fig. 1 (a) Digital map showing the regional topography of the Tu-Ha Basin and the location of the three **studied deposits** (red symbols): the Hongshan deposit, the Liuhuangshan deposit, and the Caihuagou deposit; the blue **symbol shows** the location of **the** Lianmuqin section. (b) **Simplified geological** map of the Tu-Ha Basin, **showing** the three **sampled** sites.

Fig. 2 The typical landscape in the Tu-Ha **Basin** (a: Hongshan; b: Liuhuangshan and Caihuagou); (c) **the** supergene **jarosite-enriched** weathering profiles of the Hongshan deposit; (d) Liuhuangshan deposit; (e) Caihuagou deposit; (f, g) **photographs** showing the well-crystallized jarosites present as cavity infillings; (h) **photograph** showing the pure yavapaiite intergrowth with other minerals.

Fig. 3 **Images** and photomicrographs of fine-grained (HS-20, a, b, c) **and** coarse-grained (HS-52, d, e, f) jarosite samples under **a** microscope and its SEM images (back-scattered electron) and energy dispersive spectrum **analyses**.

Fig. 4 **SEM** images (back-scattered electron) of the other jarosite samples: (a) **pseudocubic morphologies**; (b) **hexagonal pyramid morphologies**; (c) **tabular morphologies**; (d) **examples** of energy dispersive spectrum analysis results of three different morphologies **of** jarosite samples (**LHS-5, LHS-1 and CHG2-4, respectively**)

Fig. 5 **Selected** pure yavapaiite mineral **images** (a) under **optical microscope** and (b) SEM image (**back-scattered electron**) and (c) energy dispersive spectrum analyses.

Fig. 6 **Age spectra** and isochrons of the jarosite and yavapaiite samples from the Tu-Ha Basin. In **the** inverse isochron plot, the black **circles represent** the steps **that** were used to calculate the inverse isochron ages; the **blue circles represent** the steps **that** were not used to calculate the inverse isochron ages

Fig. 7 The K-Ar (Xu et al., 2008; He et al., 2009; Yang, 2013) and $^{40}\text{Ar}/^{39}\text{Ar}$ age distribution of supergene K-bearing sulfate minerals from the Tu-Ha Basin.

Fig. 8 The age distribution of supergene K-bearing sulfate minerals through a vertical profile of the Hongshan deposit. Source data: blue diamonds (this article); red diamonds (Xu et al., 2008); yellow diamond (Yang, 2013).

Table Caption

Table1 Summary of the ⁴⁰Ar/³⁹Ar ages of supergene K-bearing sulfate minerals from
the Tu-Ha Basin