

Timing and duration of supergene mineralization at the Xinrong manganese deposit, western Guangdong Province, South China: cryptomelane $^{40}\text{Ar}/^{39}\text{Ar}$ dating

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Abstract Supergene Mn-oxide deposits are widely distributed in Guangxi, Guangdong, Yunnan, and Hunan Provinces, South China, accounting for 18% of the total Mn reserves in the country. Direct dating of supergene Mn enrichment, however, is lacking. In this paper, we present high-resolution $^{40}\text{Ar}/^{39}\text{Ar}$ ages of Mn oxides from the Xinrong Mn deposit, western Guangdong, to place numerical constraints on the timing and duration of supergene Mn

enrichment. A total of ten cryptomelane samples, spanning a vertical extent of 67 m, were dated using the $^{40}\text{Ar}/^{39}\text{Ar}$ laser incremental heating technique, with seven samples yielding well-defined plateau or pseudo-plateau ages ranging from 23.48 ± 0.91 to 2.06 ± 0.05 Ma (2σ). One sample yields a staircase spectrum that does not reach a plateau; the spectrum, however, indicates the presence of two or more generations of Mn oxides in the sample, whose ages are best estimated at 22.34 ± 0.31 and 10.2 ± 0.86 Ma, respectively. The remaining two samples gave meaningless or uninterpretable results due to significant ^{39}Ar recoil and contamination by old phases. The $^{40}\text{Ar}/^{39}\text{Ar}$ data thus reveal a protracted history of weathering and supergene Mn enrichment that started at least in the end of the Oligocene or beginning of Miocene and extending into the latest Pliocene. Staircase-apparent age spectra, resulting from banded or botryoidal samples, yield an average growth rate of Mn oxides at $0.6\text{--}0.7 \times 10^{-3}$ mm kyr $^{-1}$. The values indicate that a 1-mm grain of Mn oxides may host minerals precipitated during a time span of ca. 1.5 m.y., and accumulation of Mn oxides to form economic deposits under weathering environments may take millions of years. The distribution of weathering ages shows that the oldest Mn oxides occur on the top of the profile, whereas the youngest minerals are found at the bottom, suggesting downward propagation of weathering fronts. However, two samples located at the intermediate depths of the profile yield ages comparable with those occurring at the highest elevations. Such a complexity of age distribution is interpreted in terms of preferential penetration of Mn-rich weathering solutions along more permeable fault zones, or as a result of multi stages of dissolution and re-precipitation

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of Mn oxides. A synthesis of geochronological and geological data suggests that formation of the Xinrong deposit was a consequence of a combination of favorable lithological, climatic, and structural conditions. Because the climatic and structural conditions are similar among the provinces of South China during the Cenozoic, the geochronological results obtained at Xinrong may also have implications for the timing of supergene Mn enrichment throughout South China.

Keywords $^{40}\text{Ar}/^{39}\text{Ar}$ · Cryptomelane · Supergene · Weathering · South China

Introduction

Chemical weathering and related supergene enrichment processes have produced numerous economic manganese ore deposits worldwide, providing an important source in the global manganese supply (Roy 1981; Varentsov 1996). Under some circumstances, metallic elements such as Co, Ni, Cu, Ag, Pb, Zn, and Au are also significantly enriched in supergene Mn-oxide deposits (Larson 1972; Canterford 1984; Manceau et al. 1987; Vasconcelos 1998; Quantin et al. 2002), making them more exploitable. Dating of secondary Mn oxides will provide numerical information on the timing and duration of weathering processes and supergene Mn enrichment (e.g., Vasconcelos et al. 1994; Dammer et al. 1996, 1999; Spier et al. 2006). The isotopic ages will further shed light on the factors governing the formation of supergene Mn deposits, such as paleoclimate, landscape evolution, and structures.

The potential of potassium-bearing Mn oxides (K-Mn oxides, mainly hollandite and cryptomelane) for K-Ar dating was recognized four decades ago, but only sporadic applications have been made since then (Chukhrov et al. 1966; Yashvili and Gukasyan 1972; Segev et al. 1995; Dammer et al. 1996). The large amounts of pure materials needed for K-Ar dating, the bulk analytical nature of this method, and the complex mineral assemblages intrinsic in Mn oxides have limited its applications to weathering geochronology. Vasconcelos et al. (1992, 1994) demonstrated that laser microprobe $^{40}\text{Ar}/^{39}\text{Ar}$ dating of hollandite-group minerals is ideally suitable for geochronological studies of supergene processes. The fine-scale resolution of this technique permits identification of potential argon loss and mixed phases in Mn oxides, and allows dating of multiple generations present in a single millimeter-size grain (Vasconcelos et al. 1994; Vasconcelos 1999a). In the last decade, this method has received growing interests and has been increasingly applied to the study of weathering processes, paleoclimatic reconstruction, landscape evolution, and supergene mineralization (Ruffet et

al. 1996; Hénocque et al. 1998; Dammer et al. 1999; Hautmann and Lippolt 2000; Li and Vasconcelos 2002; Carmo and Vasconcelos 2004; Colin et al. 2005; Carmo and Vasconcelos 2006; Spier et al. 2006). Existing $^{40}\text{Ar}/^{39}\text{Ar}$ studies of K-Mn oxides, however, have mainly come from Australia, Africa, Brazil, and Europe. Direct dating of Mn oxides from Asia is lacking.

China is one of the most Mn-productive countries in the world, and supergene Mn-oxide deposits account for ca. 18% of the total manganese reserves in the country (Ye et al. 1994). They are mostly distributed in the Guangxi, Guangdong, Yunnan, and Hunan Provinces, South China (Fig. 1). Prolonged chemical weathering of Late Paleozoic Mn-bearing sedimentary rocks, which are several thousands of meters thick and widespread throughout South China, has led to the formation of numerous small to medium-sized, high-grade metallurgical, and battery-active manganese ore deposits. Because of the mineralogy dominated by tetravalent manganese oxides, they are locally called Mn-oxide deposits. In most of these deposits, K-Mn oxides are abundant and their weathering-derived origin has been widely accepted (Ru et al. 1992; Hou et al. 1997).

Both Jurassic to Cretaceous and Tertiary to Quaternary ages were speculated for Mn-oxide deposits of South China, based largely on stratigraphic correlations of sedimentary rocks of approximately known ages with various continental deposits and landforms (Ru et al. 1992; Zheng 1994; Yao et al. 1995; Hou et al. 1997; Huang et al. 2001). However, direct and precise dating was not available. The abundance of cryptomelane and hollandite present in most deposits provides an excellent opportunity to directly date the timing of supergene enrichment by the $^{40}\text{Ar}/^{39}\text{Ar}$ method. In this paper, we present high-resolution $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the Xinrong Mn-oxide deposit, western Guangdong province, South China. The results suggest that intensive weathering and Mn-oxide formation started at least in the early Miocene and persisted into the latest Pliocene. The geochronological results, when combined with the geological data, are used to discuss the genesis of the Xinrong deposit.

Geological setting

The Xinrong Mn-oxide deposit is located in western Guangdong Province, 200 km west of Hong Kong (Fig. 1). The stratigraphy in the area is relatively simple and comprises three units (Fig. 2): (1) the Neoproterozoic Yunkai Group metamorphic assemblages, (2) Mid-Devonian marine sedimentary rocks, and (3) Cenozoic continental deposits. The Yunkai Group, exposed in the south and north of the mining area, consists mainly of mica quartz schist, spessartine schist, carbonaceous phyllite, and quartzite (Guangdong Bureau of Geology and Mineral Resources

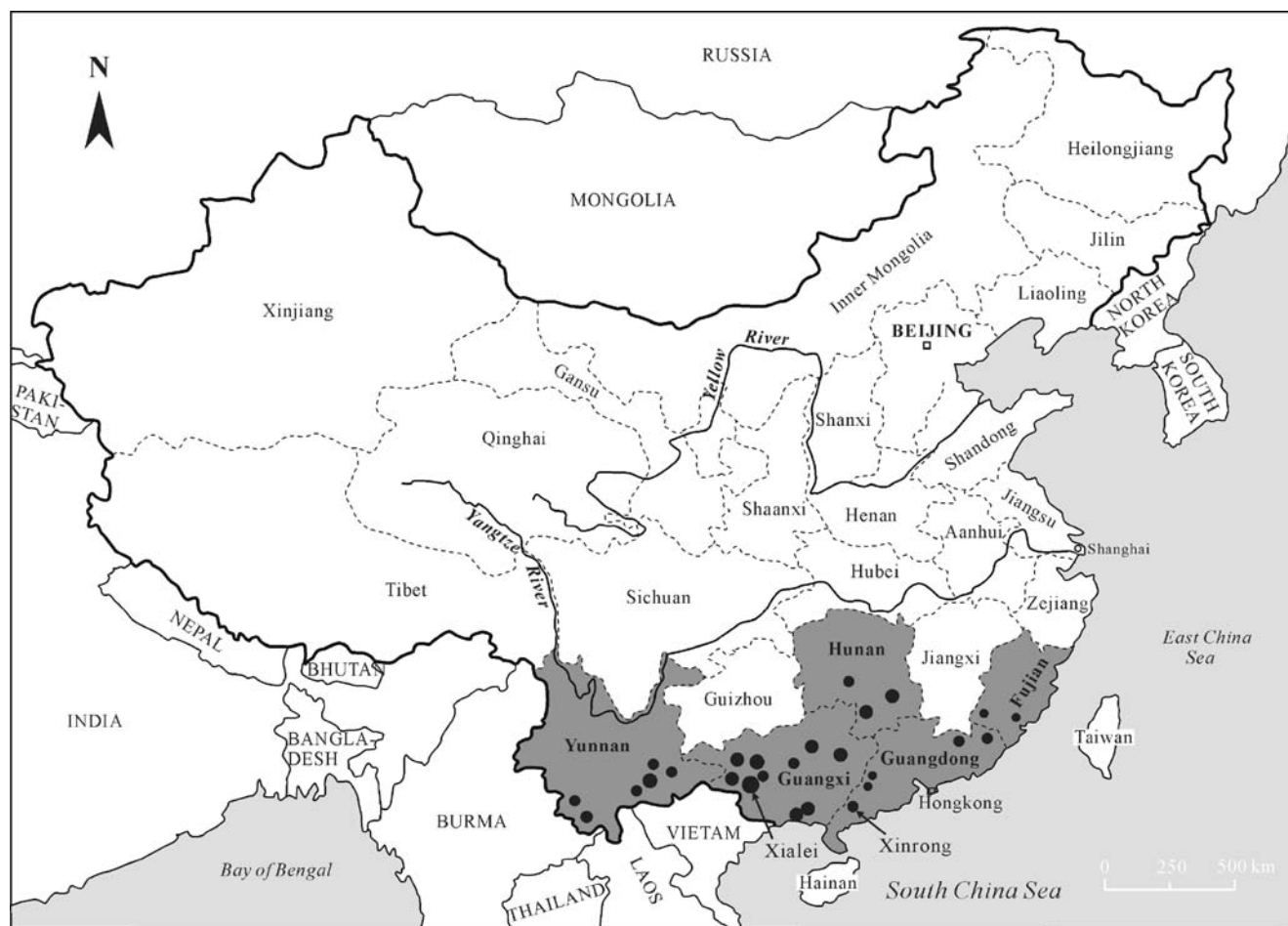


Fig. 1 Map of China showing the distribution of major supergene Mn-oxide deposits in South China. The dashed lines indicate provincial boundaries. The size of the circles denotes the relative reserves of the deposits (modified from Ru et al. 1992; Yao et al. 1995; Hou et al. 1997)

1988). The assemblages reflect upper greenschist to lower amphibolite facies metamorphism, attributed to the Caledonian orogeny of Late Silurian time that built the folded basement of South China (Yang et al. 1986). The Mid-

Devonian rocks unconformably overlie the Yunkai Group and comprise phyllites, calcareous slates, sandstones, siltstones, limestones, dolostones, and marls, with a total thickness of 1,300–1,400 m. The Cenozoic deposits are

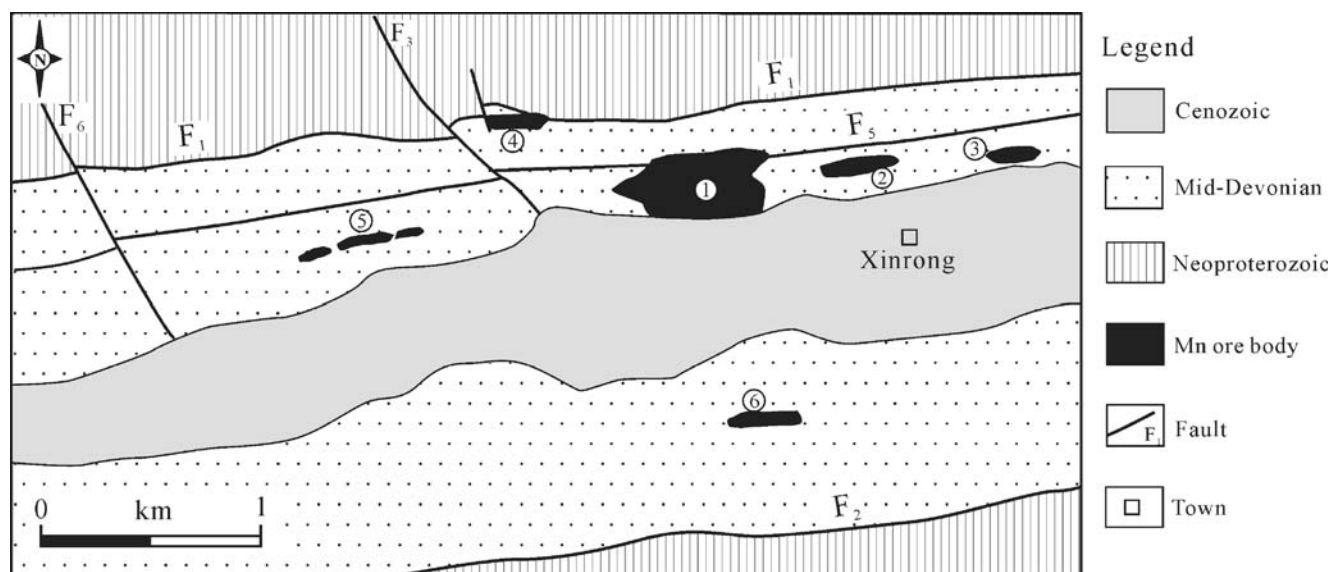


Fig. 2 Geological map of the Xinrong Mn-oxide deposit (after Huang et al. 2001). See Fig. 1 for location

highly variable in composition, thickness, and texture. Common lithologies are conglomerates, sandstones, mudstones, clay, and alluvium. These continental deposits occur mainly in depressions, low-relief plains, valleys, river terraces, and solution caves developed in the Middle Devonian rocks.

The area has a long and complex tectonic history. The main structural features include E–W trending, composite, tight folds composed of the Proterozoic metamorphic sequences that formed during the Caledonian orogeny, and ENE-oriented broad folds involving the Devonian sedimentary rocks related to the NNW–SSE oblique convergence of the Sibumasu block to the Indochina–South China blocks in the Late Permian, known as the Indosinian orogeny (Carter et al. 2001). In response to this NNW–SSE collision, regional ENE-striking thrust faults formed at the contact between the Neoproterozoic and the Middle Devonian, as revealed by the F_1 , F_2 , and F_5 faults (Fig. 2). A series of interlayered faults or intensely fractured zones were also formed accompanying the folding of the Devonian rocks. These faults were reactivated in an extensional mode due to the Cretaceous continental lithospheric extension marked by extensive magmatism and widespread basin formation over South China, known as the Yanshanian movement (Li 2000; Wang et al. 2002).

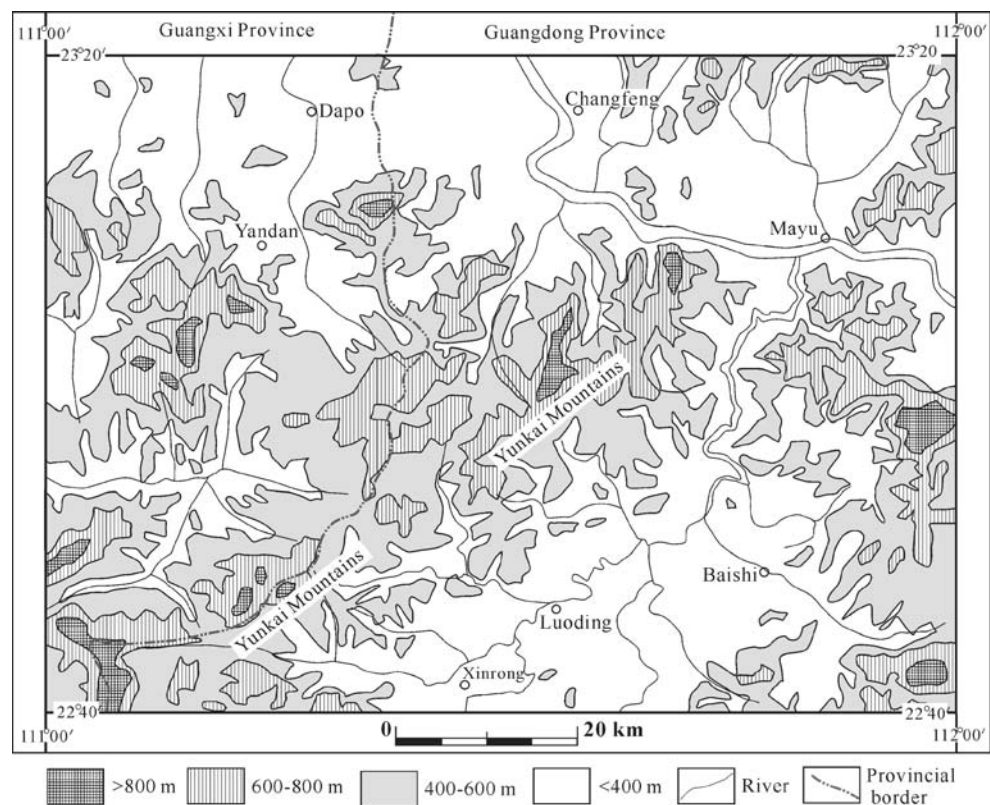
The NEE-trending faults are generally more than 15 km long at the surface, and the fracture zones are up to 80 m

wide. They are subparallel to the strike of the Devonian rocks, with a dip angle of 40–60° to the north. Late NW-oriented faults displaced the NEE-strike structures by several to a few tens of meters (Fig. 2). Several solution caves are developed, resulting from dissolution of the Devonian carbonaceous rocks. These caves are up to 40 m in depth, and have been important loci for Mn-oxide accumulation.

The region is characterized by a humid subtropical monsoonal climate, with yearly mean temperatures of 20–21°C and an average precipitation of more than 1,800 mm that mainly occurs from March to August. The warm and humid climate has led to the development of abundant and diverse vegetation, dominated by subtropical mixed broad-leaved evergreen and deciduous broad-leaved forests (Ren and Beug 2002). The landforms in the area consist of relatively flat plains and valleys at 80–120 m above sea level, separated by scattered hills ranging from 150 to 350 m in elevation (Fig. 3). A NE-striking mountainous landform ranging in elevation from 400 to 1,300 m occurs to the west of Xinrong, which is known as the Yunkai Mountain Belt (Guangdong Bureau of Geology and Mineral Resources 1988).

In the Xinrong area, the plains and valleys are covered with Cenozoic deposits and weathering profiles of variable thickness, with few exposures of the underlying rocks. The flat top hills are mantled with thin layers of ferruginous soils, overlying leached zones and saprolite of variable

Fig. 3 A simplified map showing the general geomorphology of the Xinrong area and surrounding regions (modified from Guangdong Bureau of Geology and Mineral Resources 1988)



thickness (Fig. 4a). Indurated ferruginous duricrusts, which may be impregnated by Mn oxides, were sporadically found on the hilltops (Fig. 4b). Weathering profiles are developed at the expense of both the Neoproterozoic and Devonian rocks (Fig. 4a,c). In general, the profiles are 50–70 m thick (up to 120 m in fracture zones) and mostly

consist of ferruginous duricrusts, a leached zone, saprolite, and saprock. However, some of these horizons may be absent in places. The saprolites are the most important hosts of Mn oxides (Fig. 4a,d). Supergene Fe oxides, kaolinite, and other undetermined clay minerals of variable amounts were also present throughout the weathering profiles.

Fig. 4 Photographs showing the field occurrences of Mn-oxides. **a** A flat-top hill mantled by thick weathering profiles overlying the Devonian rocks. The profile consists of thick saprolite graded upward into a leached zone overlain by a thin layer of ferruginous soil. Mn-oxides are mainly hosted in the saprolite. **b** Typical ferricrete relicts at hill tops, consisting mainly of goethite and hematite. **c** Saprocks developed on Middle Devonian carbonates. The circled areas are Mn-oxides formed during weathering of the Mn-bearing carbonates. **d** Massive Mn-oxides hosted in a saprolite zone. **e, f** Karst ores consisting of poorly crystallized and ferruginous Mn-oxides mixed with clasts of carbonates, sandstones, siltstones, and muds. **g, h** Botryoidal Mn-oxides typically found in fracture-hosted ores



Mineralization

The Xinrong Mn-oxide deposits were discovered in the late 1980s, and open-pit mining started in the mid-1990s. The deposit consists of six ore bodies (Fig. 2), of which the no. 1 ore body is the largest, occurring in a solution cave and fracture zones along the F_5 fault. Mn oxides accumulated in solution caves are locally termed karst ores, and consist of clayey ferromanganese hydroxides and nodules of Mn oxides of variable size that are mixed with abundant debris, fragments, and clasts of the Devonian carbonates and sandstones (Fig. 4e,f), which are mostly autochthonous in origin and account for ca. 20% volume of the ores. The Mn-oxide nodules are loose, poorly crystallized, highly ferruginous, and range in size from <2 mm to 50 cm. By contrast, Mn oxides hosted in fracture zones are generally compact, well crystallized, and characterized by banded, botryoidal, or massive textures (Fig. 4g,h).

Mn oxides account for >70% volume of the ore, accompanied by variable amounts of quartz, Fe oxides, and clays. The distinct features of Mn oxides from the solution caves and fracture zones may suggest different mechanisms operated during their formation. The other five ore bodies are mostly hosted in interlayered fracture zones within the Devonian rocks. They occur as dense disseminations or massive accumulations in intensely weathered zones (mostly saprolites) and infillings of open voids. Mn oxides are massive, banded, or botryoidal in texture, and generally well crystallized, indicating they formed via the mobilization of Mn into weathering solutions, followed by direct precipitation of Mn oxides in open spaces. Multiple generations of Mn oxides, indicated by distinct textures or crosscutting relationships, are noticeable.

The ores have an average grade of 22–24 wt% Mn, with a maximum of 53 wt% (Zheng 1994; Huang et al. 2001). In many cases, they also contain 10–30 wt% Fe and a maximum of 11 wt% SiO_2 (Zheng 1994; Huang et al. 2001). Concentrations of P mostly range from 0.02 to 0.08 wt%, corresponding to P/Mn ratios less than 0.003. About 0.1 Mt high-grade metallurgical manganese ores are proven, containing 40–53% Mn, a maximum of 18% Fe plus SiO_2 , and less than 0.02 wt% P.

Samples and experiments

One major difficulty in dating supergene K-Mn oxides arises from contamination of the samples of interest by the older parent materials, causing mixing and geologically meaningless or uninterpretable ages. Therefore, a basic requirement for dating these minerals is to separate samples free of contaminants. Mn oxides of botryoidal and banded textures represent direct precipitation of manganese from

weathering fluids into open spaces, and are generally devoid of contaminants. Mn oxides from the karst ores are of low purity and poor crystallinity, and therefore were not considered during the course of sampling. All samples were collected from fracture and cavity infillings of the no. 1 ore body.

We sampled at various depths through a vertical profile, attempting to discern a possible correlation between the precipitation age of Mn oxides and the depth where they precipitated. A total of ten specimens (samples) were collected over a vertical extent from 158 to 91 m in elevation. These samples, ranging in size from 4 to 10 cm, occur as botryoidal or banded concretes. They are mostly visually pure, but may locally contain variable amounts of goethite, hematite, quartz, and clays.

Polished thin sections of each sample were initially examined under reflected light using a Nikon E600 microscope. After petrographic examination, samples were crushed, washed in distilled water in an ultrasonic bath for 30–50 min, and dried. For each sample, 30–50 grains, 1–2 mm in size, were hand-picked under a binocular microscope. The purity, composition, and crystallinity of these grains were further determined by a combination of X-ray diffraction (XRD), electron microprobe (EMP) analysis, and scanning electron microscope (SEM) observation.

XRD analyses of powdered samples were performed using a Philips PW3040 series diffractometer equipped with a copper-target tube, operating at 40 kV and 40 mA. The XRD-oriented patterns were recorded using a step size of $0.02^\circ 2\theta$ and a scan speed of $1^\circ 2\theta/\text{min}$. The relative abundance of each mineral was estimated on the basis of their basal peak intensity ratio. Two to four grains from each sample were mounted in an epoxy container and polished for SEM and EMP analysis. The mounted grains were carbon-coated and investigated with a Quanta200 environmental scanning electron microscope hosted at the GPMR State Key Laboratory, China University of Geosciences.

The SEM is equipped with an energy dispersive spectrometer (EDAX GENESIS), allowing combined analysis of morphology and composition of interesting minerals. EMP analyses were done using a JEOL 733JEOL and JXA 8800R Superprobe hosted at GPMR and the Institute of Mineral Resources, Chinese Academy of Geological Sciences, respectively. Whenever possible, the microprobe analyses were programmed as traverses across growth bands in the samples to reveal the possible variation in composition.

On the basis of XRD, EMP, and SEM analyses, five to ten cryptomelane grains (1–2 mm) from each sample were loaded into aluminum irradiation disks along with Fish Canyon sanidine standards (nominal age of 28.02 ± 0.16 Ma; Renne et al. 1998), following the geometry shown in Vasconcelos (1999a). The disks were wrapped in

Al foil, vacuum-sealed in silica glass tubes, and irradiated for 14 h at the B-1 CLICIT facility at the Radiation Center, Oregon State University, USA. After a 2-month cooling period, the samples were analyzed by the laser incremental-heating $^{40}\text{Ar}/^{39}\text{Ar}$ method using a MAP215-50 noble gas mass spectrometer hosted at the Argon Geochronology Laboratory, Department of Earth Science, University of Queensland. Heating with a laser beam (Innova 300 Ar-ion laser) defocused to 2 mm diameter permitted each grain to be heated nearly homogeneously, as confirmed by visual observation of grains through a video camera. Argon gases were extracted at consecutively higher laser powers lasting for 54–62 s at each designated power.

The gases released during step heating were purified by exposing to a cryocooled trap -136°C and two C-50 Fe-Ti-Zr SAES getter pumps. The cleaned gases were then admitted into an MAP 215-50 mass spectrometer, equipped with a third getter pump, for argon isotopic analysis. During the argon analysis, a total of 22 full-system blanks and 11 air pipettes were analyzed (a blank-air-blank series before and after each grain), yielding $^{40}\text{Ar}/^{36}\text{Ar}$ discrimination values ranging from 1.0057 ± 0.0035 to 1.0053 ± 0.0034 (Appendix). Full-system blanks for ^{40}Ar range from 0.00534 ± 0.00025 to 0.00979 ± 0.00013 nA during the analysis, values considerably below the ^{40}Ar signals obtained for most gas fractions analyzed.

All dates are reported using $5.543 \times 10^{-10} \text{ year}^{-1}$ as the total decay constant for ^{40}K (Steiger and Jäger 1977), and the values for the reactor correction factors are: $(2.59 \pm 0.006) \times 10^{-4}$ for $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$, $(9.0 \pm 0.3) \times 10^{-4}$ for $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$ and $(8 \pm 3) \times 10^{-4}$ for $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$. Data corrected for blanks, mass discrimination, nucleogenic interferences, and atmospheric contamination were used to calculate apparent ages of each degassing step. The J factors were calculated from the analyses of a minimum of 15 grains of the standard placed in the irradiation disk, yielding values between 0.003657 ± 0.000020 and 0.003647 ± 0.000026 (Appendix).

Mineralogy and petrography of Mn-oxides

The integrated examinations suggest that the Mn oxides studied consist mainly of cryptomelane and pyrolusite, with subordinate amounts of hollandite, lithiophorite, nsutite, and todorokite (Figs. 5 and 6). Several modes explain the formation of cryptomelane. It may result from oxidative dissolution and replacement of primary Mn-bearing minerals (Fig. 6a,b) or occur as cements of hypogene quartz (Fig. 6c). It may also replace early-formed supergene goethite (Fig. 6d). However, cryptomelane formation was dominated by direct precipitation of Mn^{4+} into open voids from weathering solutions (Fig. 6e–g).

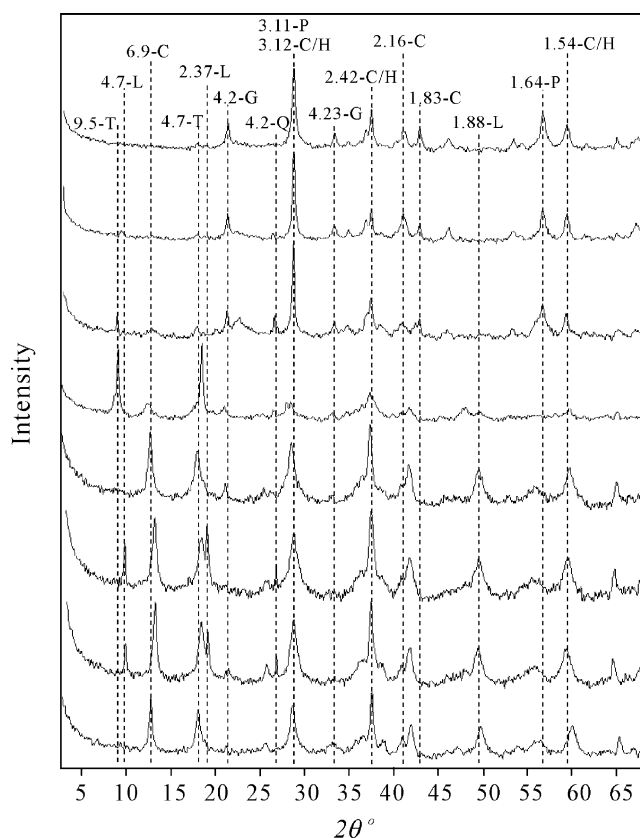
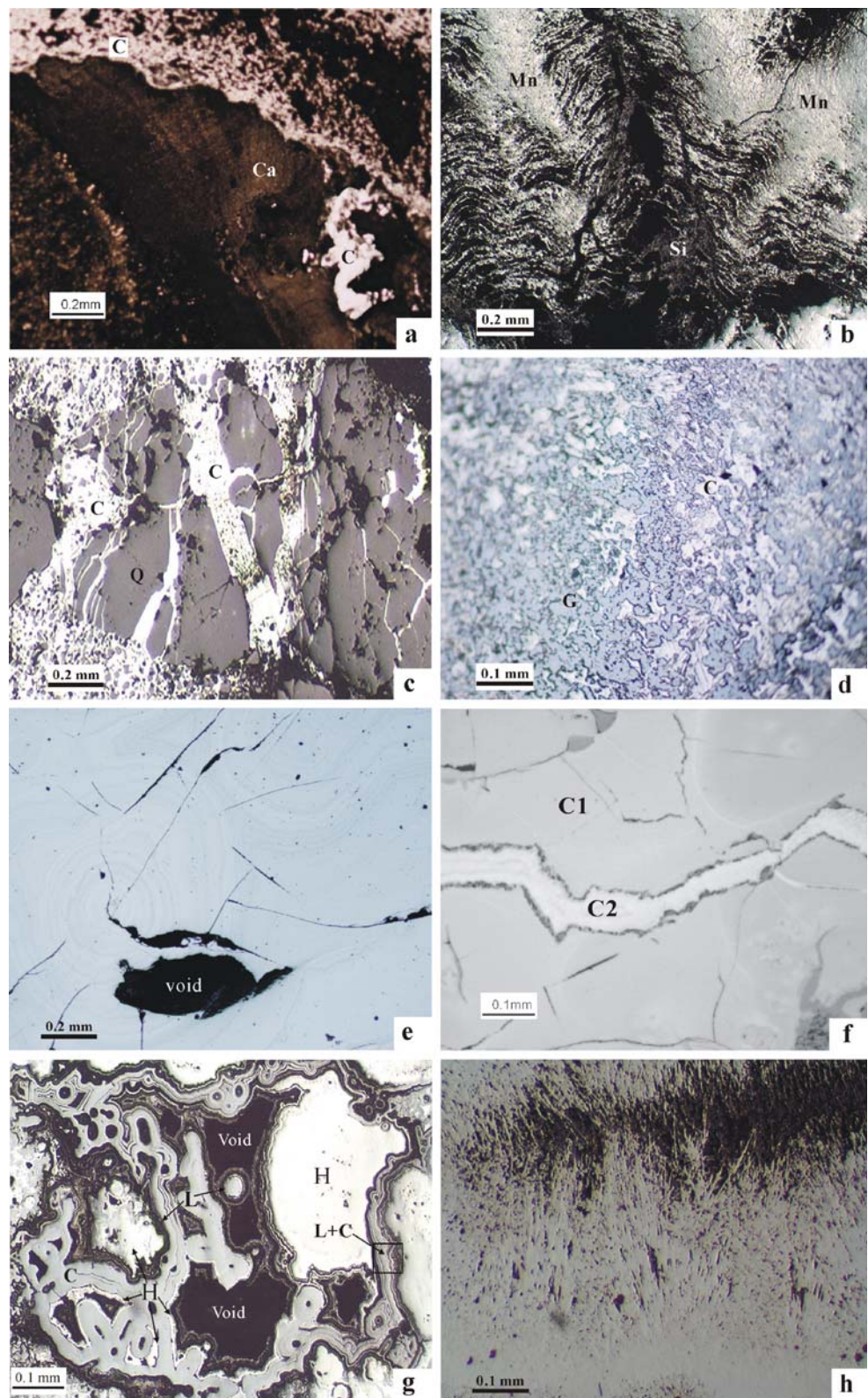


Fig. 5 Powder XRD patterns illustrating the mineralogy of Mn-oxides selected for $^{40}\text{Ar}/^{39}\text{Ar}$ dating. The number denotes the d spacing. Mineral abbreviations: C cryptomelane, H hollandite, P pyrolusite, T todorokite, L lithiophorite, G goethite, Q quartz

Void-filling cryptomelane is generally very pure, cryptocrystalline, and characterized by botryoidal or banded textures composed of micrometric growth bands (Fig. 6e). The minerals typically display a needle-like crystal form, with each crystal being 1–10 μm long and 0.5–1 μm in diameter and oriented perpendicularly to the growth bands (Fig. 7a,b). Multiple generations of cryptomelane are evident in some samples, indicating dissolution and re-precipitation of Mn oxides (Fig. 6f). Hollandite is present commonly as intergrowths with cryptomelane and lithiophorite (Fig. 6g). The textural relations, especially the acicular morphology (Fig. 6h), suggest that hollandite minerals have good crystallinity, achieved by open-space filling. Compared to cryptomelane, hollandite commonly shows higher reflectivity and a yellow reflection color (Fig. 6g), likely related to its crystal chemistry with Ba overwhelming K (see below).

Pyrolusite is a very common ore mineral, frequently exhibiting crystal faces and well-developed cleavage in hand specimen. Petrographic features, such as high reflectivity, yellow reflection color, well-developed bireflection, and strong anisotropism, make it easily recognizable under an optical microscope (Fig. 6i). It is commonly intergrown

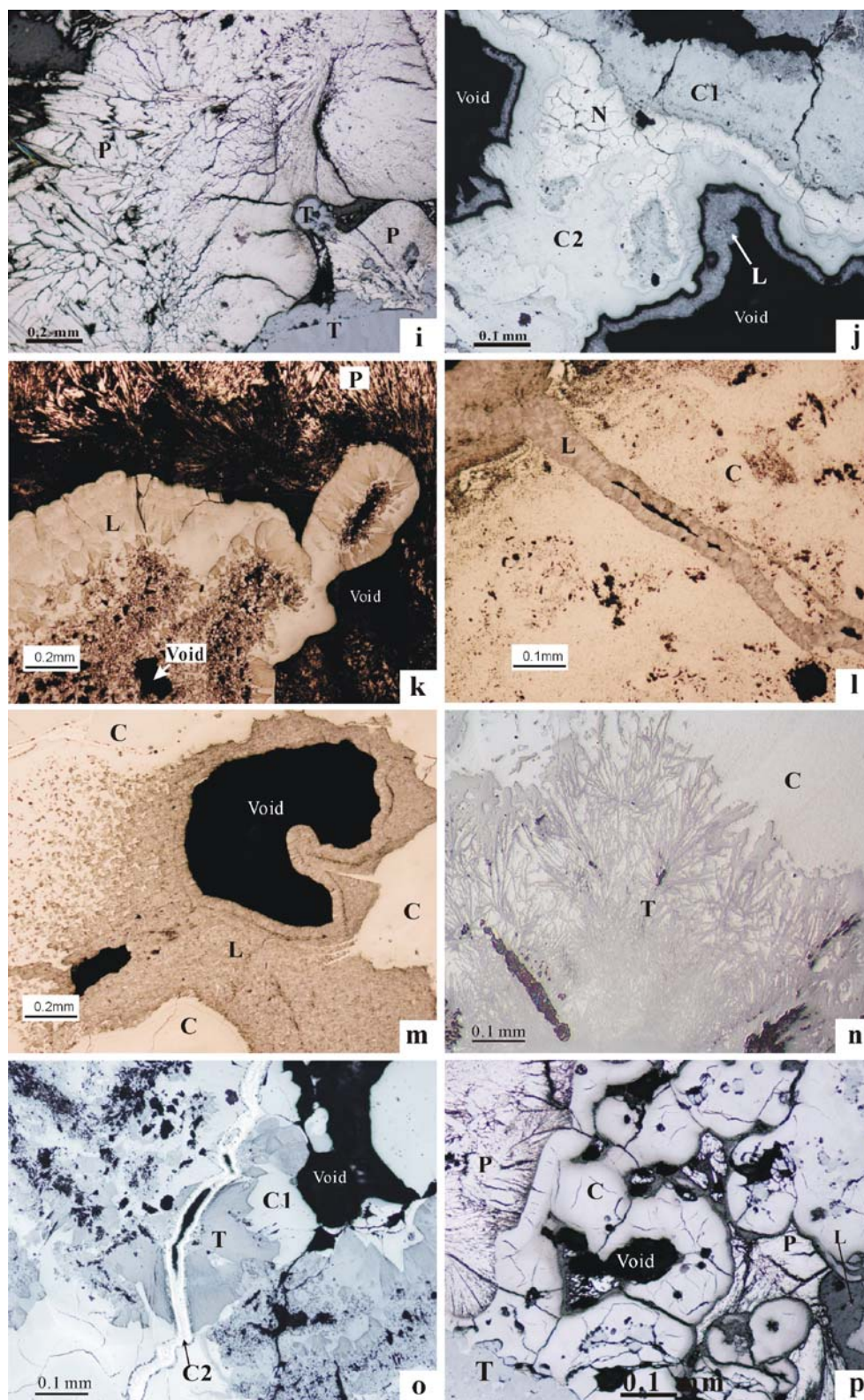
Fig. 6 Photomicrographs under reflected light showing the mineralogy and textural relationships of Mn-oxides. **a** Cryptomelane (C) replacing the Devonian primary Mn-bearing carbonate (Ca). **b** Mn-oxides (Mn) replacing hypogene silicates (Si). **c** Cryptomelane cementing quartz (Q). **d** Cryptomelane replacing goethite (G). **e** Densely botryoidal pure void-filling cryptomelane. **f** Distinct generations of cryptomelane (C1 and C2). **g** Botryoidal Mn-oxides consisting of hollandite (H), lithiophorite (L) and cryptomelane. **h** Acicular hollandite precipitated in open spaces. **i** Euhedral crystals of pyrolusite (P). Minor amounts of todorokite (T) occur as interstitial phase. **j** Nsutite (N) with typical desiccation cracks surrounded by two generations of cryptomelane (C1, C2) marked by distinct textures. Lithiophorite occurs as external layers. **k** Well-crystallized lithiophorite surrounded by pyrolusite. **l** Lithiophorite cutting through cryptomelane. **m** Cryptomelane replacing void-filling lithiophorite. **n** Todorokite replacing cryptomelane. **o** Todorokite coexisting with early stage cryptomelane (C1), but cut by late stage cryptomelane (C2). **p** Typical paragenetic relationship of Mn-oxides



with cryptomelane (Fig. 6p), but their paragenetic relationship is sometimes difficult to assess. Nsutite is also closely related to cryptomelane (Fig. 6j). There is a general idea that the absence of elements such as K, Ba, Na, and Al

causes Mn^{4+} to precipitate as nsutite and pyrolusite (Ostwald 1992). Thus, the textural relations revealed in Fig. 6 indicate frequent geochemical variation of weathering fluids.

Fig. 6 (continued)



Lithiophorite is not uncommon, and is characterized by well-developed bireflection from pearly gray to brownish gray, extreme anisotropism, but has the lowest reflectivity compared to other Mn-oxide minerals. It occurs as a fine

crystalline mass, with a sub-parallel, mica-like cleavage (Fig. 7c,d). Paragenetically, lithiophorite forms frequently as a later phase because it occurs as coatings on other minerals (Fig. 6j), occupies the innermost part of the open

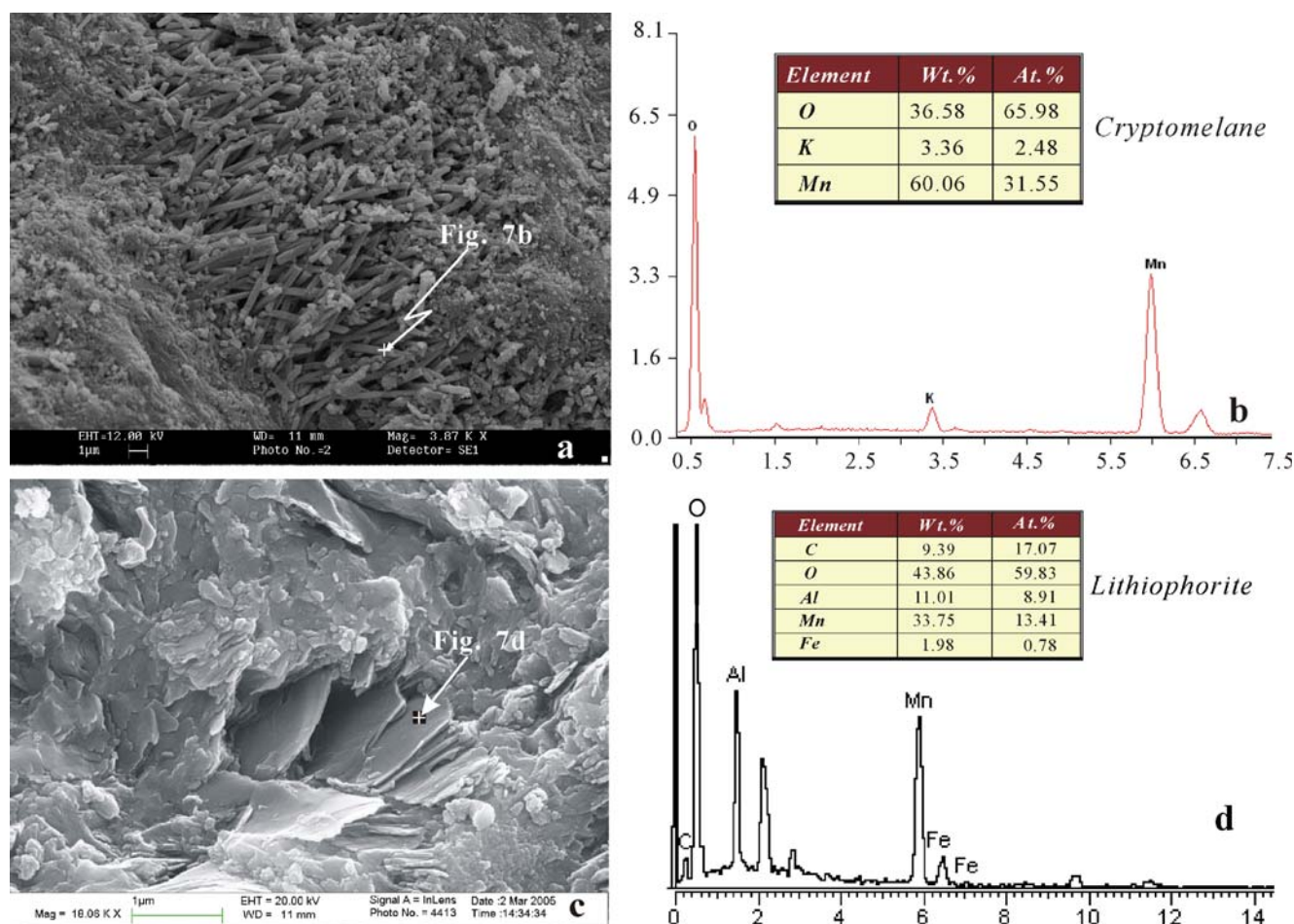


Fig. 7 SEM images and EDS analyses of cryptomelane (a, b) and lithiophorite (c, d)

space (Fig. 6k) or crosscuts other Mn-oxide minerals (Fig. 6l). However, one sample provides evidence that lithiophorite may be replaced by, and thus predate, cryptomelane (Fig. 6m). Todorokite is locally identified (Figs. 5 and 6n,o), showing fibrous or colloform textures. Todorokite may replace cryptomelane, but itself can be crosscut by late-stage cryptomelane (Fig. 6o). The complex intergrowths of various Mn oxides (Fig. 6p) make the paragenetic relations difficult to assess, and indicate dynamic changes of the geochemical and physiochemical conditions of weathering solutions.

Mineral chemistry of Mn-oxides

The averaged compositions of various Mn-oxide minerals are listed in Table 1. The contents of manganese ranges from 34 to 63 wt%, and variations of Mn concentrations reflect different mineralogy and variable occupancies of cations (Co, Al, Si, etc.) in the mineral structures. Cryptomelane contains up to 5 wt% K, with an average of 2.28 wt%. Barium is low in cryptomelane, usually less than 1 wt%. Hollandite is characterized by high Ba

Table 1 Average composition of Mn-oxide minerals

	Cm n=168	Hol n=19	Py n=51	Li n=34	Tod n=15
Na	0.06	0.04	0.01	0.02	0.23
K	2.28	0.48	0.13	0.13	0.24
Mn	57.02	48.70	61.77	39.29	51.68
O	33.64	32.98	35.16	43.39	39.12
Ca	0.17	0.12	0.02	0.02	0.98
Fe	0.30	1.06	0.36	0.60	0.42
Al	0.95	1.31	0.21	10.97	0.33
Si	0.08	0.11	0.18	0.32	0.09
P	0.08	0.34	0.18	0.03	0.12
Co	0.02	0.09	n.d.	0.14	0.01
Ni	0.03	0.06	0.01	0.56	0.09
Pb	0.01	0.00	n.d.	0.02	n.d.
Zn	0.08	0.07	0.02	0.47	0.02
Cu	0.07	0.03	n.d.	0.27	n.d.
Ba	0.24	9.41	0.05	0.01	0.46
Total	95.04	94.80	98.10	96.24	93.79

Some analyses, where both Ba and K are moderately high, were not included in the calculation of the average compositions of Cm and Hol;

Cm cryptomelane, Hol hollandite, Py pyrolusite, Li lithiophorite, Tod todorokite, n.d. not detected

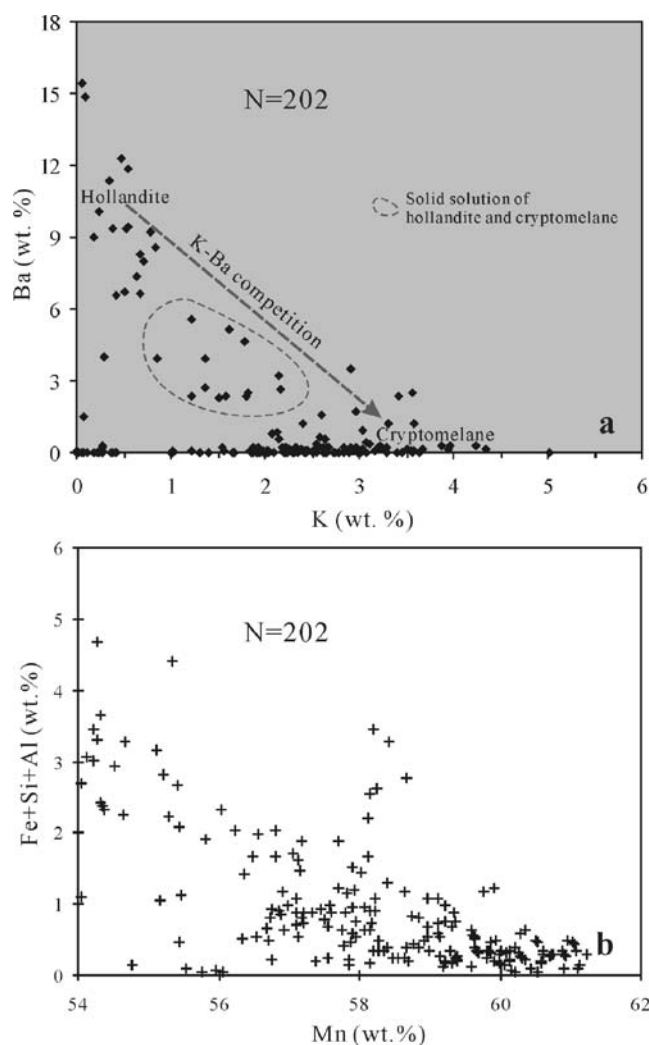


Fig. 8 K–Ba (a) and Mn–Fe+Si+Al (b) correlations revealed by EMP analyses of hollandite-group minerals

concentration (up to 15.4 wt%) and low K (0.48 wt% on average; Table 1). The K–Ba correlations, based on 202 spot analyses (Fig. 8a), indicate that cryptomelane and hollandite may coexist as a solid solution (Burns and Burns 1979).

Both cryptomelane and hollandite contain some amounts of Fe, Si, P, and Al (Table 1), and the Mn vs Al+Si+Fe diagram (Fig. 8b) reveals competition between these elements for the tunnel sites. Because nsutite and pyrolusite cannot be distinguished through EMP analysis, we regard all analyses characterized by high Mn (generally >60 wt%), but very low trace elements, as pyrolusite. Compared to other Mn oxides, pyrolusite (nsutite) has the highest Mn (61.8 wt% on average), but lowest trace element contents (Table 1). Lithiophorite typically contains 8–16 wt% Al and some amounts of Si, Fe, Co, Ni, Cu, and Zn (Table 2). The metal elements Co, Ni, Cu, and Zn in lithiophorite, albeit low, are highest among the minerals identified.

Todorokite contains variable amounts of Na, K, Ba, Ca, Fe, P, and Al, with Cu and Pb below the detection limit. Closely intergrown with Mn oxides, goethite contains 60–64 wt% Fe, accompanied by Mn, Al, Si, and P, with total contents less than 4 wt% (not shown in Table 1). Phosphorus tends to be incorporated into Fe oxides, rather than Mn oxides, whenever these minerals coexist.

The EMP analyses indicate that weathering solutions from which Mn oxides were precipitated are rich in Mn, Fe, Al, K, and Ba, together with some amounts of Ca, Na, Si, Cu, and base metals. However, the composition of weathering solutions, notably in terms of trace elements, seems highly variable during the formation of Mn oxides, as revealed by EMP traverses of millimeter-size Mn-oxide grains consisting of micrometric bands (Fig. 9). A dynamic change of component of weathering solutions is also indicated by the complex paragenesis (Fig. 6).

$^{40}\text{Ar}/^{39}\text{Ar}$ age results

Full analytical data are tabulated in Appendix, and a summary of $^{40}\text{Ar}/^{39}\text{Ar}$ ages is reported in Table 2 and illustrated graphically in Fig. 10. In this study, a plateau is defined as a sequence of three or more continuous steps that contain more than 60% of the total amount of ^{39}Ar released

Table 2 Summary of $^{40}\text{Ar}/^{39}\text{Ar}$ ages of supergene Mn-oxides at the Xinrong Mn deposit, South China

Sample	Elevation (m)	Plateau age (Ma)	$\pm 2\sigma$	Integrated age (Ma)	$\pm 2\sigma$	Isochron age (Ma)	$\pm 2\sigma$	Intercept $^{40}\text{Ar}/^{36}\text{Ar}$	$\pm 2\sigma$	Comments
XR-04	158	23.48 ^a	0.91	31.4	1.30	n.a.	n.a.	n.a.	n.a.	^{39}Ar recoil
XR-10	151	22.34 ⁺	0.31	20.9	0.30	n.a.	n.a.	n.a.	n.a.	Staircase spectra
XR-16	146	16.03	0.19	14.8	0.20	15.5	0.20	278	9	Plateau
XR-20	140	13.4	0.14	13.7	0.30	13.32	0.15	301	4	Plateau
XR-21	133	21.6 ^a	0.40	31.5	0.40	n.a.	n.a.	n.a.	n.a.	^{39}Ar recoil
XR-22	125	21.76 ^a	1.95	24.4	0.60	23.86	1.43	310	12	Staircase spectra
XR-25	96	2.46	0.11	2.69	0.19	2.44	0.13	302	6	Plateau
XR-26	91	2.06	0.05	2.23	0.09	2.02	0.07	306	10	Plateau

Samples XR-01 and XR-29 were not included. Ages with (^a) are pseudo plateau ages. Age with (+) is a weighted mean age. n.a. not applicable

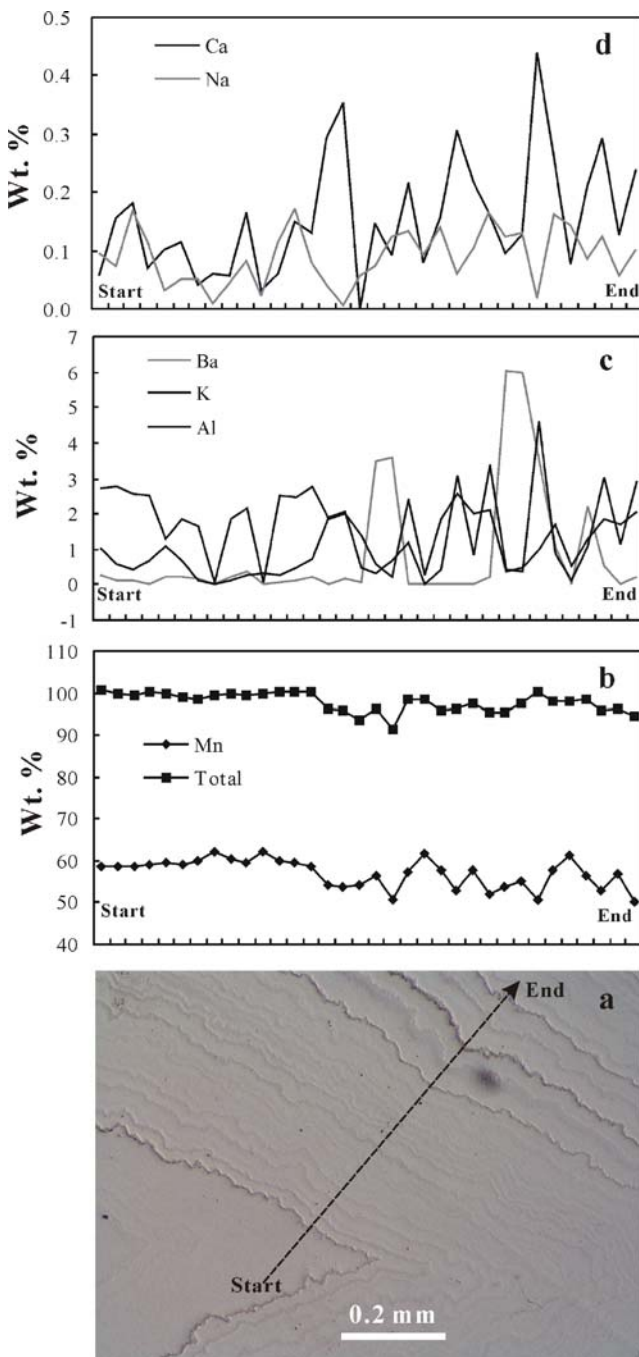


Fig. 9 **a** Photomicrograph illustrating an EMP traverse through Mn-oxide growth bands. **b–d** Manganese and trace elemental abundances through these bands are highly variable

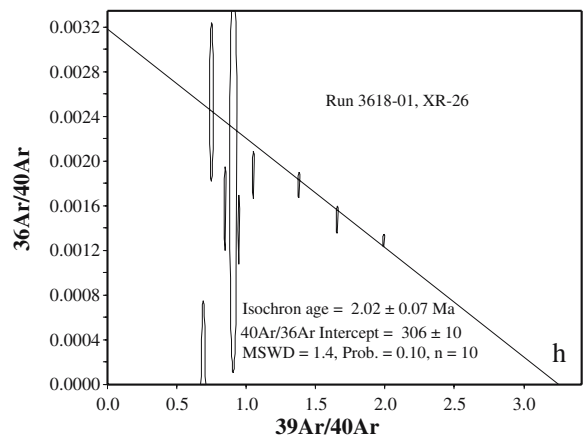
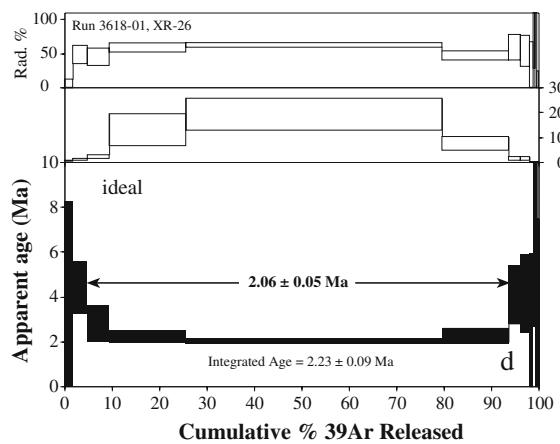
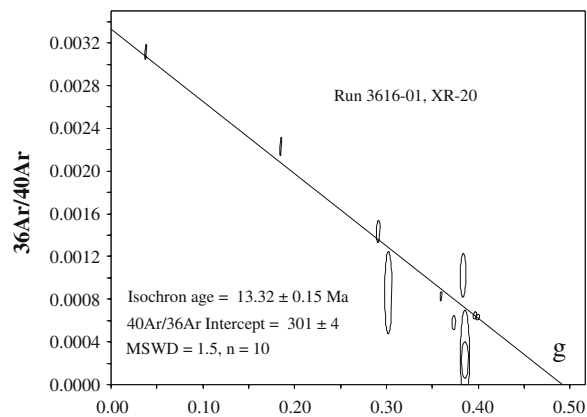
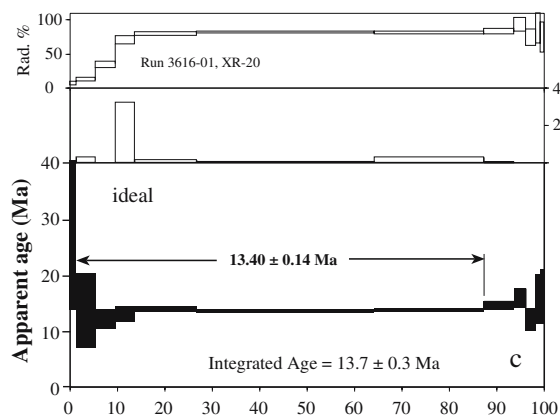
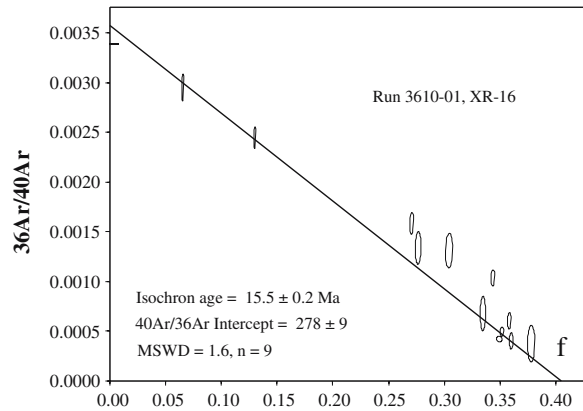
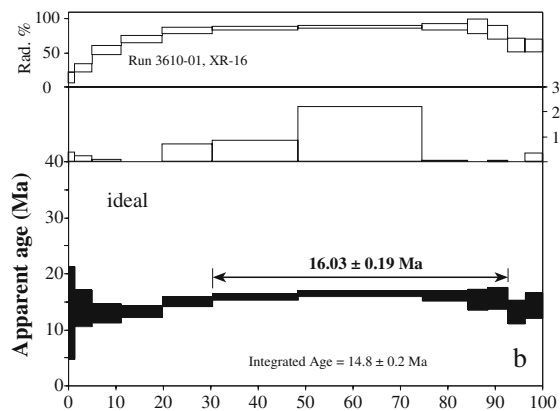
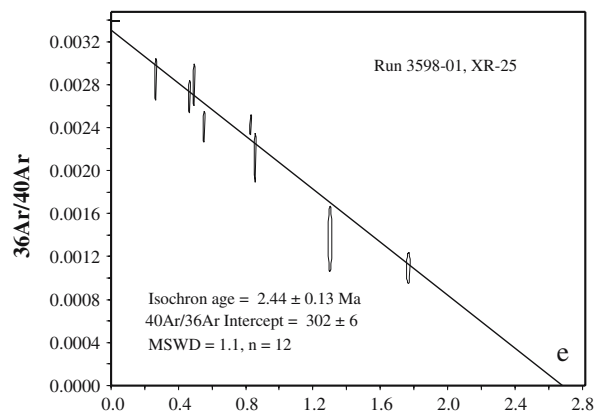
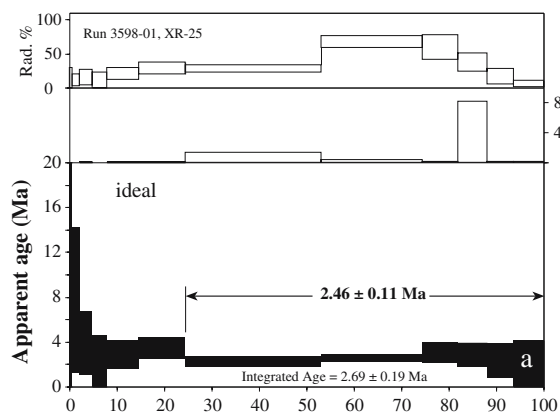
and yields apparent ages reproducible at the 95% confidence level (2σ). A pseudo-plateau is defined as a sequence of two or more steps containing more than 50% of the total ^{39}Ar released, but the age values of each step are only reproducible at the 90% confidence level (2σ), or containing slightly less than 50% of the total amount of ^{39}Ar released that yield results reproducible at the 95% confidence level (2σ).

Fig. 10 $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra and isochrons of selected Mn-oxide samples

Four samples yield well-defined plateau ages (Fig. 10a–d), ranging from 16.03 ± 0.19 to 2.06 ± 0.05 Ma. Characteristics of these spectra suggest that ^{39}Ar loss by recoil, contamination by old minerals, argon loss by cation exchange with surrounding groundwaters and atmosphere, and inherited argon resulted from decomposition of parent minerals (Vasconcelos 1999a) did not occur in these samples. Therefore, the plateau ages are reliably interpreted as true precipitation age for the samples. Plots of $^{39}\text{Ar}/^{40}\text{Ar}$ vs $^{36}\text{Ar}/^{40}\text{Ar}$ yield isochron ages consistent with the respective plateau ages (Fig. 10e–h). The isochrons have initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of 306 ± 10 to 278 ± 9 , indistinguishable from the present-day atmospheric value (295.5) and indicating absence of excess argon in the samples.

The fine-scaled nature of cryptomelane growth bands (10–30 μm ; Fig. 6e–g) prevented the separation of homogeneous fragments from a single generation for dating. When the grains contain multiple generations that possess variable thermal stability, incremental heating analyses will result in staircase spectra (Fig. 10i,j). In the case of sample XR-10 (Fig. 10i), two mid-high temperature steps (steps D and E), which account for 65% of the total ^{39}Ar released, yield descending apparent ages at 23.64 ± 0.29 and 20.62 ± 0.33 Ma, respectively (Fig. 10i). Subsequent three high-temperature steps (steps F–H) yield an internally concordant but much younger apparent age at 10.2 ± 0.86 Ma. Thus, this spectrum represents a mixture of two or more distinct phases, which are intimately intergrown, and the younger phase is better crystallized and more retentive of $^{40}\text{Ar}^*$ than the older phase. The weighted mean age from steps D and E is 22.34 ± 0.31 Ma, which may be considered as the average of the age of the older phase. Despite the fact that the spectrum does not reach a plateau, it may still contain valid geochronological information (Vasconcelos and Conroy 2003). Sample XR-22 yields an ascending spectrum that defines a pseudo-plateau age at 21.76 ± 1.95 Ma, which is interpreted to represent the mean age of precipitation for the growth bands in the sample. The present staircase spectra also permit a calculation for the average precipitation rate of Mn oxides at $0.6\text{--}0.7 \times 10^{-3} \text{ mm kyr}^{-1}$, consistent with previously estimated results (Hénocque et al. 1998; Dammer et al. 1999; Li and Vasconcelos 2002). The values suggest that a 1-mm grain of banded Mn oxide may host minerals precipitated during a time span of ca. 1.5 m.y., indicating that long periods (tens of million years) are needed to form economic supergene Mn deposits (Vasconcelos 1999a).

^{39}Ar loss by recoil is not uncommon in $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of Mn oxides (Vasconcelos 1999b), mainly



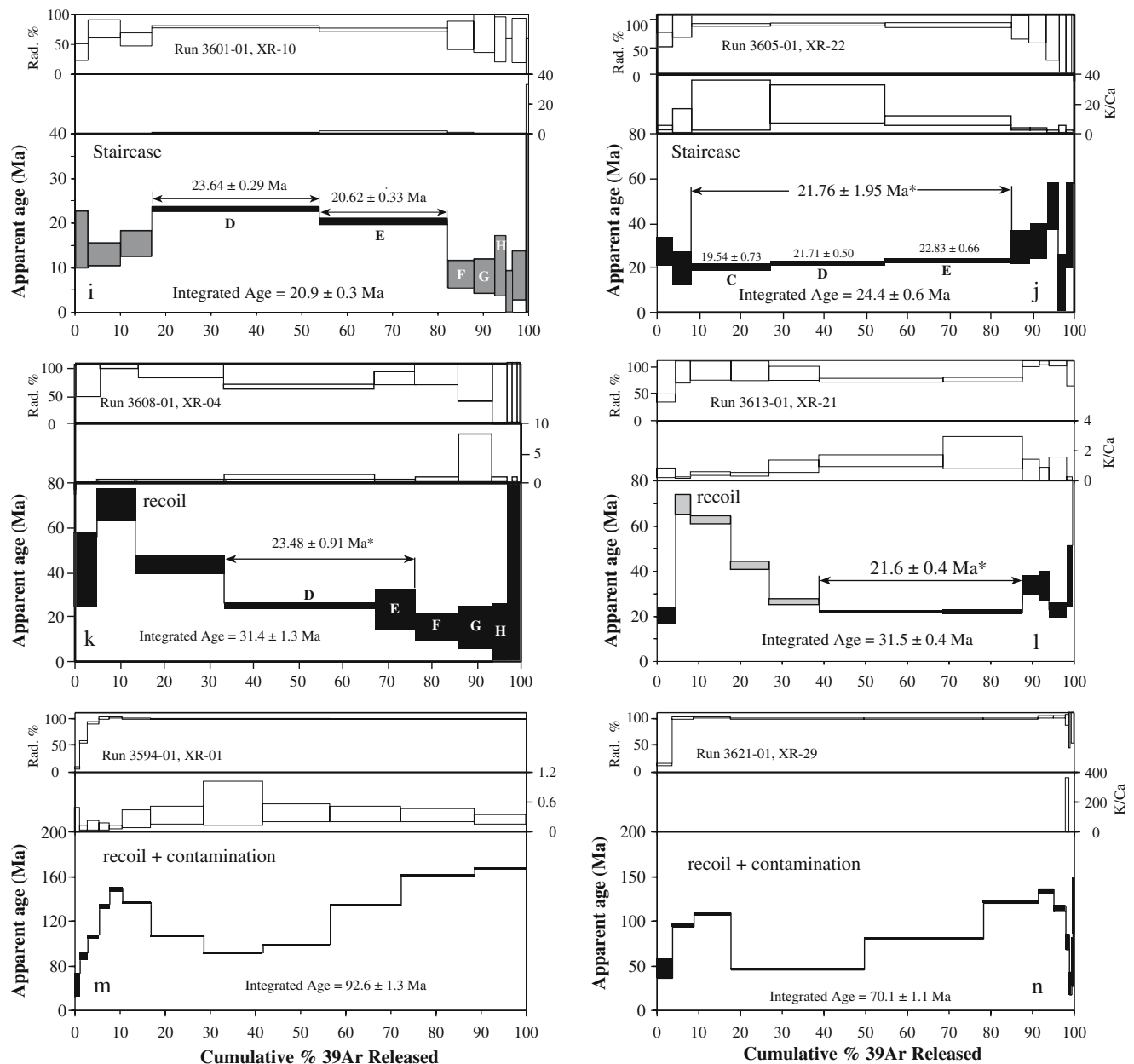


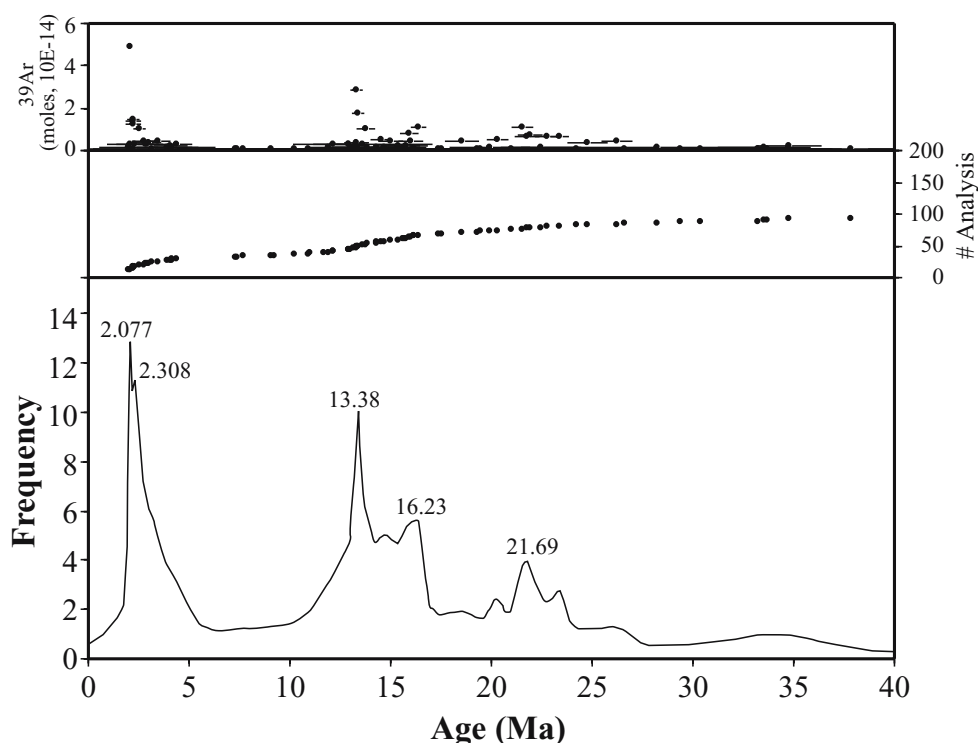
Fig. 10 (continued)

due to the very fine-grained nature of the minerals (<1–2 μm ; Fig. 7a). When significant ^{39}Ar loss occurs, reliable age information on the samples cannot be retrieved. However, if only a minor amount of ^{39}Ar is lost by recoil, a plateau or pseudo-plateau age may still be obtained (Vasconcelos 1999a). Figure 10k,l illustrates spectra for samples that appear to have ^{39}Ar recoil during neutron irradiation and/or bake-out procedure. The spectra are characterized by anomalously old apparent ages in the low-temperature steps, which decrease at progressively higher temperatures and reach a pseudo-plateau defined by the mid-high temperature steps. The pseudo-plateau ages are

23.48 ± 0.91 and 21.6 ± 0.4 Ma, respectively, being the best estimates for the ages of these samples.

Two samples (XR-01 and XR-29) yield complex spectra that do not reach plateau or pseudo-plateau (Fig. 10m,n). The spectra resulted from a combination of old contaminants intergrown with the supergene Mn oxides and significant ^{39}Ar loss by recoil. Geologically meaningful age information cannot be retrieved from these spectra. This suggests that old contaminants, despite great caution, were not fully avoided for these samples. This further indicates that careful sample preparation is essential for successfully dating Mn oxides by the $^{40}\text{Ar}/^{39}\text{Ar}$ method (Vasconcelos 1999a).

Fig. 11 An ideogram plotted using samples yielding plateau or pseudo plateau ages, illustrating the distribution of precipitation ages of Mn oxides



Discussion

Timing of supergene Mn enrichment

Seven of ten Mn-oxide samples yield well-defined plateau or pseudo-plateau ages ranging from 23.48 ± 0.91 to 2.06 ± 0.05 Ma, revealing a prolonged history of weathering and supergene manganese enrichment from the latest Oligocene to latest Pliocene (Fig. 11). However, the present geochronological results provide only a minimum constraint on the timing and duration of supergene mineralization at the Xinrong deposit. Such a view is based on the consideration that erosion has been an active process while weathering proceeds, so that the oldest supergene minerals precipitated at the early stage of weathering have been very likely eroded, leading to incomplete records of the weathering history. This is consistent with the fact that most weathering profiles in the area are dominated by a truncated saprolite zone. Moreover, open-pit mining operations, which started in the mid 1990s, have removed the upper part of the weathering profiles where old supergene minerals were hosted, and thus precluded the possibility to date the onset of weathering and precipitation of Mn-oxides.

Considering these factors, we suggest that weathering and supergene Mn enrichment at Xinrong may have prevailed throughout the Oligocene. Geochemical and isotopic studies of marine sediments at the ODP site 1148 in the South China Sea indicate an abrupt increase in the intensity of chemical weathering in south China since

29.5 Ma (Li et al. 2003), supporting an Oligocene weathering event.

Likewise, the youngest ages (2.46–2.06 Ma) of Mn oxides do not necessarily imply that precipitation of supergene Mn oxides at Xinrong ceased in the latest Pliocene, as samples from the lowermost part of the ore bodies have not been available. From a geochemical point of view, weathering is favored by the availability of meteoric solutions and high water/rock ratios, and significant accumulations of supergene Mn oxides are facilitated by intense weathering under wet and warm climates (Vasconcelos 1999a). Therefore, the Quaternary humid subtropical climate in the area (Hu et al. 2003; Tougard and Montuire 2006) should continue to cause weathering of Mn-bearing rocks, and consequent precipitation of supergene Mn oxides. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Xialei Mn-oxide deposit from Guangxi (Fig. 1), the largest Mn deposit in China, with demonstrated economic resources of 134 Mt (Yao et al. 1995), provides evidence for intense weathering and Mn-oxide formation spanning the entire Quaternary (till 0.3 Ma; Yan 2006). Given that the Xinrong and Xialei areas have had similar climatic conditions during the Quaternary, we propose that Quaternary supergene Mn mineralization should have also been active at Xinrong.

Whether chemical weathering and related supergene enrichment of Mn oxides are continuous or episodic is still a matter of controversy (Vasconcelos et al. 1994; Ruffet et al. 1996; Dammer et al. 1999). Continuous or episodic precipitation of Mn oxides essentially reflects the climatic

conditions under which these supergene minerals form. Discrete episodes of Mn-oxide precipitation could have been related to alteration between more humid and drier climates in the past, whereas continuous precipitation may result from a relatively stable climate conducive to leaching and transport of manganese. The age probability diagram plotted using samples yielding plateau or pseudo-plateau ages reveals four major peaks at 2.31–2.08, 13.38, 16.23, and 21.69 Ma (Fig. 11). The presence of multiple age peaks may lead one to propose that weathering at Xinrong has been episodic.

Nevertheless, it is premature to draw such a conclusion, because the existence of multiple age peaks may simply reflect a sampling bias: only ten samples were dated in this study, which is obviously insufficient to unravel the whole history of weathering and supergene mineralization in the region (Vasconcelos et al. 1994; Vasconcelos 1999a). Considering that South China has experienced a wet subtropical climate since the early Miocene or late Oligocene (see below), it may be appropriate to assume a continuous scenario for weathering and supergene Mn enrichment in the region. On the other hand, petrographic observations reveal occurrences of multiple generations of Mn oxides (Fig. 6), indicating dissolution and re-precipitation of Mn oxides, processes presumably related to alternating climatic conditions (Dammer et al. 1999; Vasconcelos 1999a). At this stage, we emphasize that more detailed sampling and systematic isotopic dating are required to examine whether supergene Mn-enrichment at Xinrong is continuous or episodic.

Weathering fronts propagate downwards, causing inverse correlation between the age and location of supergene minerals. In this case, older weathering ages are envisaged for samples present at the top of weathering profiles, with progressively younger ages at increasing depths (Vasconcelos 1999b; Vasconcelos and Conroy 2003). Basically, this is reflected in our samples that record the downward migration of the weathering fronts from earliest Miocene to latest Pliocene. The samples located at the highest elevations (158–151 m) yield the oldest, earliest Miocene ages of 23.48–22.34 Ma (Fig. 12). In the lower part of the profile (96- and 91-m elevations), samples yield the youngest, latest Pliocene age of 2.46–2.06 Ma (Fig. 12).

Between these, samples XR-16 and XR-20, which are located at elevations of 146 and 140 m, respectively, yield mid-Miocene ages of 16.03 and 13.4 Ma, respectively (Fig. 12). However, samples XR-21 and XR-22, located at intermediate depths of the profile (133–125 m), yield ages similar to those from samples at the highest elevations (Fig. 12). A possible explanation for such a complexity of weathering age distribution is that the weathering fronts were undulated due to preferential penetration of Mn-rich weathering fluids along more permeable fault zones, so that

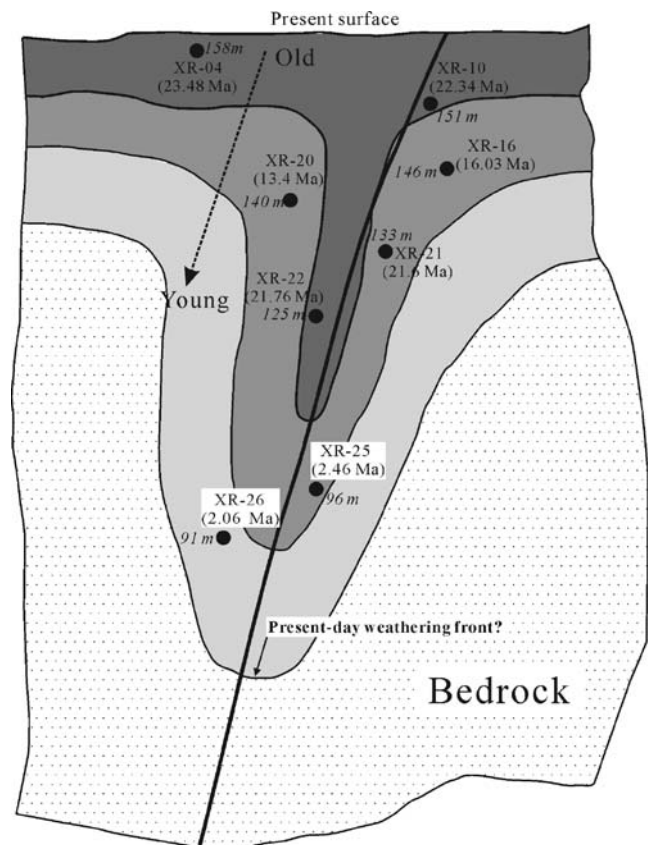


Fig. 12 Age distribution of supergene Mn-oxides at Xinrong through a vertical profile. Not to scale

Mn oxides were synchronously precipitated at various depths within the profile (e.g., Vasconcelos 1999b). Alternatively, such an age distribution may have arisen from multi-stage dissolution and re-precipitation of Mn-oxide minerals during the supergene enrichment.

Genesis of the Xinrong Mn-oxide deposit

Large accumulation of supergene Mn oxides results from the interactions of oxidized meteoric waters with Mn-bearing precursor rocks under an optimum combination of lithological, climatic, and structural factors (Varentsov 1996). Field occurrences (Fig. 4a,c–e) and petrographic observations (Fig. 6a–c) suggest that Mn oxides at the Xinrong deposit were derived from weathering of the Neoproterozoic and Devonian rocks. These rocks contain Mn ranging from 1.5 to 16.2 wt% (Yao et al. 1995; Huang et al. 2001), constituting important Mn sources for the deposit. However, the field relations of Mn oxides to the host rocks are complex and, in many instances, direct geochemical relationships between these two cannot be discerned, as shown by numerous Mn-oxide veins or nodules hosted in the Devonian sandstones and shales that are extremely low in Mn (Huang et al. 2001). This indicates that, in many cases, manganese must have experienced

significant lateral transport after release from the parent rocks.

While Mn-bearing lithologies provide a source of supergene Mn oxides, the weathering-prone climate throughout the Neogene time was the most important factor that led to the development of Mn oxides. After long-standing aridity spanning from the Late Cretaceous to the end of the Eocene, South China was dominated by a humid climate after the beginning of the Oligocene, and notably during the Miocene (Wang 1984; Liu et al. 1998). The protracted wet climate is reflected by the widespread occurrences of lignite and oil shales in a number of inland and marginal sea basins of Late Cenozoic age in Guangdong and adjacent Provinces (Wang 1990; Yao et al. 1995). It is also indicated by abundant and diversified fossil floras from these basins, which reflect evergreen broad-leaved forests of Neogene age throughout South China (Song et al. 1983; Wang 1989). Marine transgression during the Miocene and significant development of carbonate platforms in the marginal sea basins of South China further indicate the prevalence of a warm regime during that time period (Guangdong Bureau of Geology and Mineral Resources 1988).

The long-term humid and hot climate provided sufficient meteoric waters to leach, transport, and deposit Mn. A wet and warm climate is also favorable for the development of vegetation and organic matter, which affect Mn-oxide formation likely by two mechanisms (Crerar et al. 1972; Drever 1994; Varentsov 1996). The first is the direct influence of plants on the physical and hydrological properties of weathering fronts by modifying water residence times, and thus the contact and interaction time between primary minerals and aqueous solutions. The second is the chemical influence induced by the production of organic acids from plant roots, microorganisms, and by microbial decay of dead plants. Organic acids favor chemical weathering by increasing acidity, thereby promoting the dissolution of both primary Mn-bearing minerals and early-precipitated Mn oxides, as demonstrated by crosscutting relationship between different generations of Mn oxides (Fig. 6).

A recent study of apatite and zircon fission track thermochronology reveals that large areas in western Guangdong have experienced significant uplift since the Early Cretaceous, notably from Late Cretaceous to the Oligocene (97–33 Ma; Li et al. 2005). Intensive uplift is indicated by the exhumation of high-grade metamorphism and mylonites in the Yunkai Mountain Belt, immediately west of Xinrong (Fig. 3). This uplift is thought to be related to lithospheric extension coupled with asthenospheric upwelling that was active during most of the Cretaceous in South China (Li 2000). Long-term uplift contributed to exposing the Mn-bearing protoliths, being attacked by oxidized and acid ground waters. Multi-stage deformation related to the Caledonian and Indosinian orogenies and the Yanshanian

movement, which affected all of southeastern China, further enhanced the permeability of the Proterozoic and Devonian rocks. Oxidizing meteoric solutions penetrated preferentially along the folded bedding planes, faulted zones, and interlayered fractures, promoting decomposition of the Mn-bearing carbonates and silicates in the source rocks (Fig. 6a–c). The structures also advanced the development of solution caves in the Devonian carbonates, which, together with the faulted zones, acted as important loci for Mn-oxide deposition. The preferential penetration of weathering solutions along fault zones may have also caused complex age distributions of Mn oxides through vertical profiles (Fig. 12).

In summary, the Xinrong Mn-oxide deposit may have formed by the following processes: (1) metamorphism of the Yunkai Group and formation of Mn-bearing silicates (spessartine) during the Late Silurian Caledonian orogeny, (2) deposition of Devonian Mn carbonates within a shallow-marine environment; (3) deformation of Proterozoic and Devonian rocks during the Indosinian orogeny and the Yanshanian movements that enhanced permeability of these Mn-bearing rocks; (4) uplift since the Late Mesozoic causing exposure of the Mn-containing rocks; and (5) weathering and supergene enrichment starting at least in the earliest Miocene or, more likely, in the Oligocene, under a humid subtropical climate.

Conclusions

$^{40}\text{Ar}/^{39}\text{Ar}$ dating of cryptomelane from the Xinrong Mn-oxide deposit (South China) yields well-defined plateau or pseudo-plateau ages ranging from 23.48 ± 0.91 to 2.06 ± 0.05 Ma, and thus reveals prolonged weathering and supergene Mn mineralization lasting from the latest Oligocene through to the latest Pliocene. However, supergene Mn enrichment may date back to the early Oligocene and extend into the Quaternary, given that samples from both the uppermost and lowest part of the weathering profiles were not available for study. The precipitation ages of Mn oxides show a general correlation with their location along a vertical profile, where old Mn oxides generally occur at the top, whereas younger minerals formed at progressively great depths, indicating downward propagation of weathering fronts. Old weathering ages identified from intermediate-depth samples may reflect preferential penetration of Mn-rich weathering solutions along more permeable faults or fracture zones, or result from multiple events of dissolution and re-precipitation of Mn oxides. The formation of the Xinrong Mn-oxide deposit has been jointly controlled by the distribution of Mn-bearing parent rocks, the long-term uplift resulting in exposure of the protoliths, multiple stages of deformation that facilitated percolation of

oxidizing fluids, and the humid climate that probably started in the Oligocene and contributed to dissolution and transport of manganese and ultimately the deposition of Mn oxides. Because the climatic and structural conditions are similar among the provinces of South China, where Mn-bearing sedimentary rocks are widespread, the geochronological results obtained at Xinrong may also have implications for the timing of supergene Mn enrichments throughout South China.

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Appendix

Table 3

Table 3 $^{40}\text{Ar}/^{39}\text{Ar}$ analytical results of supergene Mn oxides at the Xinrong manganese ore deposit, South China

Run_ID	Sample	$^{40}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}^*/^{39}\text{Ar}$	Age	$\pm 2\sigma$	^{39}Ar (Moles)	^{40}Ar (Moles)	^{40}Ar (nA)	^{39}Ar (nA)	J $\pm 2\sigma$	Laser (W)	$^{40}\text{Ar}/^{36}\text{Ar}$ discr.	
3594-01A	XR-01	55.040	0.040	5.800	0.167	6.080	11.01	39.60	5.70	2.98E-15	1.64E-13	5.953	0.108	0.003647 $\pm$ 0.000026	0.10	1.0053
3594-01B	XR-01	14.975	0.011	5.500	0.002	14.890	99.04	95.39	0.99	3.99E-15	5.97E-14	2.170	0.145	0.003647 $\pm$ 0.000026	0.20	1.0053
3594-01C	XR-01	16.984	0.012	4.800	0.001	17.130	100.54	109.34	0.88	6.98E-15	1.19E-13	4.307	0.254	0.003647 $\pm$ 0.000026	0.30	1.0053
3594-01D	XR-01	7.381	0.011	0.860	0.001	7.272	98.47	47.22	0.29	2.48E-14	1.83E-13	6.663	0.903	0.003647 $\pm$ 0.000026	0.35	1.0053
3594-01E	XR-01	12.806	0.012	0.790	0.001	12.608	98.41	81.10	0.40	2.23E-14	2.85E-13	10.363	0.809	0.003647 $\pm$ 0.000026	0.40	1.0053
3594-01F	XR-01	19.125	0.011	4.030	0.001	19.150	99.87	121.81	0.75	1.03E-14	1.97E-13	7.167	0.375	0.003647 $\pm$ 0.000026	0.45	1.0053
3594-01G	XR-01	20.750	0.011	6.300	0.001	21.110	101.27	133.80	1.50	2.95E-15	6.13E-14	2.227	0.107	0.003647 $\pm$ 0.000026	0.50	1.0053
3594-01H	XR-01	17.530	0.012	4.700	0.000	17.930	101.90	114.30	1.50	2.21E-15	3.87E-14	1.406	0.080	0.003647 $\pm$ 0.000026	0.55	1.0053
3594-01I	XR-01	11.840	0.013	25.700	-0.001	14.300	118.50	91.70	5.90	6.82E-16	8.08E-15	0.294	0.025	0.003647 $\pm$ 0.000026	0.60	1.0053
3594-01J	XR-01	5.319	0.007	62.000	0.001	10.400	188.00	67.40	8.40	4.74E-16	2.52E-15	0.092	0.017	0.003647 $\pm$ 0.000026	0.80	1.0053
3594-01K	XR-01	10.030	0.010	-55.000	-0.005	7.000	72.00	45.00	14.00	2.09E-16	2.10E-15	0.076	0.008	0.003647 $\pm$ 0.000026	1.00	1.0053
3594-01L	XR-01	20.370	0.012	-51.000	-0.002	16.400	83.00	105.00	16.00	2.15E-16	4.38E-15	0.159	0.008	0.003647 $\pm$ 0.000026	2.00	1.0053
3598-01A	XR-25	10.890	0.015	1.100	0.032	1.530	14.10	10.10	5.60	2.88E-16	3.13E-15	0.114	0.010	0.003657 $\pm$ 0.000020	0.10	1.0057
3598-01B	XR-25	10.850	0.016	0.420	0.033	1.210	11.10	7.90	3.10	7.50E-16	8.14E-15	0.296	0.027	0.003657 $\pm$ 0.000020	0.20	1.0057
3598-01C	XR-25	3.712	0.012	-0.030	0.011	0.610	16.30	4.00	1.30	1.21E-15	4.50E-15	0.164	0.044	0.003657 $\pm$ 0.000020	0.30	1.0057
3598-01D	XR-25	3.002	0.015	0.920	0.009	0.310	10.40	2.10	1.20	1.51E-15	4.54E-15	0.165	0.055	0.003657 $\pm$ 0.000020	0.35	1.0057
3598-01E	XR-25	2.119	0.013	-0.020	0.006	0.437	20.60	2.88	0.58	3.17E-15	6.72E-15	0.245	0.115	0.003657 $\pm$ 0.000020	0.40	1.0057
3598-01F	XR-25	1.787	0.013	0.610	0.004	0.517	28.90	3.41	0.47	4.63E-15	8.27E-15	0.301	0.168	0.003657 $\pm$ 0.000020	0.45	1.0057
3598-01G	XR-25	1.199	0.012	-0.058	0.003	0.339	28.30	2.23	0.20	1.37E-14	1.64E-14	0.596	0.497	0.003657 $\pm$ 0.000020	0.50	1.0057
3598-01H	XR-25	0.558	0.011	0.007	0.001	0.380	68.20	2.51	0.15	1.01E-14	5.62E-15	0.204	0.366	0.003657 $\pm$ 0.000020	0.55	1.0057
3598-01I	XR-25	0.741	0.012	0.290	0.001	0.446	60.30	2.94	0.40	3.62E-15	2.68E-15	0.097	0.132	0.003657 $\pm$ 0.000020	0.60	1.0057
3598-01J	XR-25	1.130	0.013	-0.780	0.002	0.419	37.10	2.76	0.46	2.88E-15	3.26E-15	0.118	0.105	0.003657 $\pm$ 0.000020	0.80	1.0057
3598-01K	XR-25	1.983	0.013	-0.280	0.006	0.330	16.60	2.17	0.72	2.64E-15	5.24E-15	0.191	0.096	0.003657 $\pm$ 0.000020	1.00	1.0057
3598-01L	XR-25	5.507	0.016	0.000	0.018	0.290	5.20	1.90	0.99	3.04E-15	1.67E-14	0.609	0.111	0.003657 $\pm$ 0.000020	2.00	1.0057
3601-01A	XR-10	6.740	0.011	6.200	0.016	2.600	38.40	17.00	2.90	5.00E-16	3.37E-15	0.123	0.018	0.003657 $\pm$ 0.000020	0.10	1.0057
3601-01B	XR-10	2.615	0.014	5.480	0.003	2.210	84.30	14.50	1.20	1.24E-15	3.23E-15	0.118	0.045	0.003657 $\pm$ 0.000020	0.20	1.0057
3601-01C	XR-10	4.057	0.014	1.480	0.006	2.420	59.50	15.90	1.40	1.18E-15	4.77E-15	0.174	0.043	0.003657 $\pm$ 0.000020	0.30	1.0057
3601-01D	XR-10	3.730	0.011	0.990	0.001	3.606	96.60	23.64	0.29	6.31E-15	2.35E-14	0.856	0.229	0.003657 $\pm$ 0.000020	0.35	1.0057
3601-01E	XR-10	3.317	0.011	0.320	0.001	3.143	94.80	20.62	0.33	4.83E-15	1.60E-14	0.582	0.176	0.003657 $\pm$ 0.000020	0.40	1.0057
3601-01F	XR-10	2.010	0.012	5.480	0.002	1.800	89.00	11.80	1.40	9.93E-16	2.00E-15	0.073	0.036	0.003657 $\pm$ 0.000020	0.45	1.0057
3601-01G	XR-10	1.783	0.015	1.600	0.002	1.410	79.00	9.30	1.70	7.90E-16	1.41E-15	0.051	0.029	0.003657 $\pm$ 0.000020	0.50	1.0057
3601-01H	XR-10	2.752	0.014	3.800	0.004	1.960	71.00	12.90	3.00	4.24E-16	1.17E-15	0.042	0.015	0.003657 $\pm$ 0.000020	0.55	1.0057
3601-01I	XR-10	2.385	0.018	4.900	0.008	0.370	16.00	2.50	5.10	2.33E-16	5.56E-16	0.020	0.008	0.003657 $\pm$ 0.000020	0.60	1.0057
3601-01J	XR-10	2.244	0.010	3.600	0.003	1.620	72.00	10.60	2.40	5.17E-16	1.16E-15	0.042	0.019	0.003657 $\pm$ 0.000020	1.00	1.0057
3601-01K	XR-10	12.310	0.024	-0.300	0.026	4.600	37.00	30.00	14.00	9.24E-17	1.14E-15	0.041	0.003	0.003657 $\pm$ 0.000020	2.00	1.0057
3605-01A	XR-22	6.594	0.015	15.700	0.013	4.080	61.20	26.60	3.20	9.80E-16	6.46E-15	0.238	0.036	0.003647 $\pm$ 0.000026	0.10	1.0053
3605-01B	XR-22	2.607	0.016	8.600	0.001	2.910	111.00	19.00	3.80	1.00E-15	2.62E-15	0.097	0.037	0.003647 $\pm$ 0.000026	0.20	1.0053
3605-01C	XR-22	2.776	0.012	2.800	0.000	2.890	89.80	19.54	0.73	4.33E-15	1.20E-14	0.443	0.159	0.003647 $\pm$ 0.000026	0.30	1.0053
3605-01D	XR-22	3.237	0.011	2.590	0.000	3.319	90.36	21.71	0.50	6.23E-15	2.02E-14	0.744	0.230	0.003647 $\pm$ 0.000026	0.35	1.0053
3605-01E	XR-22	3.234	0.011	6.000	0.000	3.620	87.27	22.83	0.66	6.94E-15	2.24E-14	0.827	0.256	0.003647 $\pm$ 0.000026	0.40	1.0053
3605-01F	XR-22	2.954	0.011	23.000	0.001	4.440	100.20	29.00	3.70	1.07E-15	3.16E-15	0.117	0.039	0.003647 $\pm$ 0.000026	0.45	1.0053
3605-01G	XR-22	2.724	0.012	25.900	0.000	4.810	106.33	31.40	3.90	9.76E-16	2.66E-15	0.098	0.036	0.003647 $\pm$ 0.000026	0.50	1.0053
3605-01H	XR-22	3.177	0.013	50.100	0.000	7.270	108.90	47.20	5.40	5.77E-16	1.83E-15	0.068	0.021	0.003647 $\pm$ 0.000026	0.55	1.0053
3605-01I	XR-22	3.115	0.015	-14.000	0.003	1.000	132.00	6.50	9.50	3.97E-16	1.24E-15	0.046	0.015	0.003647 $\pm$ 0.000026	0.60	1.0053

Table 3 (continued)

Run_ID	Sample	$^{40}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}^*/^{39}\text{Ar}$	% $^{40}\text{Ar}^*$	Age	$\pm 2\sigma$	^{39}Ar (Moles)	^{40}Ar (Moles)	^{40}Ar (nA)	^{39}Ar (nA)	J $\pm 2\sigma$	Laser (W)	$^{40}\text{Ar}/^{36}\text{Ar}$ discret.
3605-01J	XR-22	3.042	0.011	49.000	0.004	5.800	185.00	38.00	9.60	4.02E-16	1.22E-15	0.045	0.015	0.003647 $\pm$ 0.000026	0.80	1.0053
3605-01K	XR-22	3.290	0.037	380.000	0.012	40.000	890.00	240.00	100.00	6.14E-17	2.02E-16	0.007	0.002	0.003647 $\pm$ 0.000026	1.00	1.0053
3605-01L	XR-22	8.290	0.039	900.000	0.016	200.000	890.00	990.00	570.00	3.50E-17	2.90E-16	0.011	0.001	0.003647 $\pm$ 0.000026	2.00	1.0053
3608-01A	XR-04	7.963	0.016	41.000	0.017	6.300	77.00	41.00	8.30	5.43E-16	4.33E-15	0.159	0.020	0.003647 $\pm$ 0.000026	0.10	1.0053
3608-01B	XR-04	9.525	0.013	21.200	0.002	10.720	110.80	69.20	3.90	8.93E-16	8.51E-15	0.314	0.033	0.003647 $\pm$ 0.000026	0.20	1.0053
3608-01C	XR-04	4.843	0.013	22.200	0.001	6.520	102.50	42.40	2.10	2.06E-15	9.96E-15	0.367	0.076	0.003647 $\pm$ 0.000026	0.30	1.0053
3608-01D	XR-04	3.429	0.012	5.800	0.000	3.800	71.30	23.80	0.87	3.44E-15	1.18E-14	0.435	0.127	0.003647 $\pm$ 0.000026	0.35	1.0053
3608-01E	XR-04	2.365	0.013	19.200	0.001	3.530	83.40	23.10	4.80	8.93E-16	2.11E-15	0.078	0.033	0.003647 $\pm$ 0.000026	0.40	1.0053
3608-01F	XR-04	1.861	0.012	10.300	0.001	2.310	103.00	15.10	3.00	1.02E-15	1.91E-15	0.070	0.038	0.003647 $\pm$ 0.000026	0.45	1.0053
3608-01G	XR-04	1.940	0.010	3.300	0.000	2.280	117.00	14.90	4.70	7.45E-16	1.45E-15	0.053	0.027	0.003647 $\pm$ 0.000026	0.50	1.0053
3608-01H	XR-04	2.415	0.012	-10.000	0.001	1.300	55.00	8.70	8.30	3.56E-16	8.60E-16	0.032	0.013	0.003647 $\pm$ 0.000026	0.55	1.0053
3608-01I	XR-04	3.190	0.020	81.000	0.006	8.200	240.00	53.00	48.00	1.02E-16	3.26E-16	0.012	0.004	0.003647 $\pm$ 0.000026	0.60	1.0053
3608-01J	XR-04	2.519	0.018	33.000	0.003	4.400	170.00	28.00	35.00	1.25E-16	3.16E-16	0.012	0.005	0.003647 $\pm$ 0.000026	0.80	1.0053
3608-01K	XR-04	2.650	0.040	210.000	0.032	12.000	370.00	75.00	76.00	4.98E-17	1.32E-16	0.005	0.002	0.003647 $\pm$ 0.000026	1.00	1.0053
3608-01L	XR-04	17.200	0.020	190.000	0.042	23.000	110.00	140.00	210.00	1.69E-17	2.92E-16	0.011	0.001	0.003647 $\pm$ 0.000026	2.00	1.0053
3610-01A	XR-16	15.350	0.022	1.200	0.046	1.770	11.50	11.60	3.90	5.48E-16	8.41E-15	0.306	0.020	0.003647 $\pm$ 0.000026	0.10	1.0057
3610-01B	XR-16	7.661	0.015	0.130	0.019	2.030	26.50	13.30	1.50	1.62E-15	1.24E-14	0.451	0.059	0.003647 $\pm$ 0.000026	0.20	1.0057
3610-01C	XR-16	3.688	0.013	-0.120	0.006	1.910	51.70	12.50	0.78	2.59E-15	9.56E-15	0.348	0.094	0.003647 $\pm$ 0.000026	0.30	1.0057
3610-01D	XR-16	2.903	0.013	-0.300	0.003	1.979	68.20	12.97	0.48	3.78E-15	1.10E-14	0.399	0.137	0.003647 $\pm$ 0.000026	0.35	1.0057
3610-01E	XR-16	2.782	0.012	0.420	0.002	2.248	80.80	14.73	0.42	4.53E-15	1.26E-14	0.459	0.165	0.003647 $\pm$ 0.000026	0.40	1.0057
3610-01F	XR-16	2.835	0.013	0.270	0.002	2.402	84.70	15.73	0.27	7.69E-15	2.18E-14	0.793	0.280	0.003647 $\pm$ 0.000026	0.45	1.0057
3610-01G	XR-16	2.855	0.011	0.010	0.001	2.487	87.11	16.29	0.20	1.12E-14	3.21E-14	1.168	0.409	0.003647 $\pm$ 0.000026	0.50	1.0057
3610-01H	XR-16	2.763	0.012	-0.200	0.001	2.387	86.40	15.63	0.41	4.11E-15	1.13E-14	0.413	0.149	0.003647 $\pm$ 0.000026	0.55	1.0057
3610-01I	XR-16	2.603	0.011	-0.630	0.001	2.210	84.90	14.47	0.81	1.86E-15	4.83E-15	0.176	0.068	0.003647 $\pm$ 0.000026	0.60	1.0057
3610-01J	XR-16	2.942	0.014	-0.470	0.002	2.240	76.10	14.66	0.87	1.83E-15	5.37E-15	0.195	0.066	0.003647 $\pm$ 0.000026	0.80	1.0057
3610-01K	XR-16	3.222	0.012	-0.690	0.005	1.820	56.50	11.93	0.93	1.57E-15	5.06E-15	0.184	0.057	0.003647 $\pm$ 0.000026	1.00	1.0057
3610-01L	XR-16	3.543	0.013	-0.060	0.005	1.980	55.80	12.96	0.99	1.53E-15	5.41E-15	0.197	0.056	0.003647 $\pm$ 0.000026	2.00	1.0057
3613-01A	XR-21	7.382	0.014	9.200	0.018	2.810	37.80	18.40	2.20	1.58E-15	1.17E-14	0.430	0.058	0.003647 $\pm$ 0.000026	0.10	1.0053
3613-01B	XR-21	8.934	0.014	26.100	0.003	10.350	113.80	66.90	2.20	1.35E-15	1.20E-14	0.444	0.050	0.003647 $\pm$ 0.000026	0.20	1.0053
3613-01C	XR-21	9.066	0.011	10.500	0.001	9.680	106.00	62.58	0.95	3.50E-15	3.18E-14	1.171	0.129	0.003647 $\pm$ 0.000026	0.30	1.0053
3613-01D	XR-21	5.724	0.012	11.400	0.001	6.500	101.60	42.26	0.91	3.30E-15	1.89E-14	0.695	0.121	0.003647 $\pm$ 0.000026	0.35	1.0053
3613-01E	XR-21	3.750	0.011	8.100	0.000	4.340	86.50	28.34	0.85	4.28E-15	1.60E-14	0.591	0.158	0.003647 $\pm$ 0.000026	0.40	1.0053
3613-01F	XR-21	3.179	0.012	1.780	0.001	3.148	74.90	21.60	0.50	1.07E-14	3.40E-14	1.254	0.395	0.003647 $\pm$ 0.000026	0.45	1.0053
3613-01G	XR-21	3.474	0.011	1.980	0.001	3.478	75.40	22.74	0.68	6.82E-15	2.37E-14	0.874	0.251	0.003647 $\pm$ 0.000026	0.50	1.0053
3613-01H	XR-21	4.519	0.015	16.900	0.000	5.840	128.00	38.10	3.20	1.46E-15	6.61E-15	0.244	0.054	0.003647 $\pm$ 0.000026	0.55	1.0053
3613-01I	XR-21	3.767	0.009	16.100	-0.001	5.500	144.00	35.80	4.50	8.48E-16	3.19E-15	0.118	0.031	0.003647 $\pm$ 0.000026	0.60	1.0053
3613-01J	XR-21	2.884	0.012	8.600	0.000	3.490	120.00	22.80	2.50	1.53E-15	4.42E-15	0.163	0.056	0.003647 $\pm$ 0.000026	0.80	1.0053
3613-01K	XR-21	3.085	0.015	59.000	0.001	7.800	241.00	50.00	10.00	4.96E-16	1.53E-15	0.056	0.018	0.003647 $\pm$ 0.000026	1.00	1.0053
3613-01L	XR-21	5.220	0.012	84.000	-0.009	15.200	274.00	97.00	17.00	1.80E-16	9.42E-16	0.035	0.007	0.003647 $\pm$ 0.000026	2.00	1.0053
3616-01A	XR-20	64.520	0.050	0.160	0.203	4.600	7.10	30.10	7.80	1.03E-15	6.64E-14	2.416	0.037	0.003647 $\pm$ 0.000026	0.10	1.0057
3616-01B	XR-20	26.170	0.026	-0.200	0.081	2.110	8.10	13.80	3.30	3.02E-15	7.90E-14	2.874	0.110	0.003647 $\pm$ 0.000026	0.20	1.0057
3616-01C	XR-20	5.421	0.014	0.330	0.012	1.870	34.60	12.29	0.82	3.23E-15	1.75E-14	0.636	0.117	0.003647 $\pm$ 0.000026	0.30	1.0057
3616-01D	XR-20	3.429	0.010	-0.200	0.005	2.000	58.20	13.08	0.66	3.10E-15	1.06E-14	0.386	0.113	0.003647 $\pm$ 0.000026	0.35	1.0057
3616-01E	XR-20	2.783	0.012	-0.007	0.002	2.107	75.70	13.81	0.25	1.00E-14	2.79E-14	1.016	0.365	0.003647 $\pm$ 0.000026	0.40	1.0057

3616-01F	XR-20	2.502	0.013	0.137	0.002	2.035	81.36	13.34	0.13	2.85E-14	7.14E-14	2.595	1.038	0.003647±0.000026	0.45	1.0057
3616-01G	XR-20	2.524	0.012	-0.024	0.002	2.041	80.90	13.38	0.17	1.76E-14	4.44E-14	1.614	0.640	0.003647±0.000026	0.50	1.0057
3616-01H	XR-20	2.674	0.013	0.050	0.002	2.219	83.00	14.54	0.36	4.80E-15	1.28E-14	0.467	0.175	0.003647±0.000026	0.55	1.0057
3616-01I	XR-20	2.577	0.011	1.790	0.001	2.400	93.00	15.72	0.77	1.96E-15	5.06E-15	0.184	0.071	0.003647±0.000026	0.60	1.0057
3616-01J	XR-20	2.589	0.011	0.620	0.003	1.790	69.00	11.72	0.93	1.55E-15	4.02E-15	0.146	0.056	0.003647±0.000026	0.80	1.0057
3616-01K	XR-20	2.552	0.011	0.120	0.001	2.300	90.00	15.10	2.00	6.95E-16	1.77E-15	0.065	0.025	0.003647±0.000026	1.00	1.0057
3616-01L	XR-20	3.260	0.010	-0.900	0.003	2.330	71.00	15.20	2.20	6.13E-16	2.00E-15	0.073	0.022	0.003647±0.000026	2.00	1.0057
3618-01A	XR-26	9.772	0.018	4.250	0.032	0.540	5.50	3.50	2.00	1.63E-15	1.59E-14	0.579	0.059	0.003647±0.000026	0.10	1.0057
3618-01B	XR-26	1.369	0.012	2.110	0.003	0.615	44.90	4.04	0.55	2.85E-15	3.90E-15	0.142	0.103	0.003647±0.000026	0.20	1.0057
3618-01C	XR-26	0.946	0.012	0.970	0.002	0.389	41.10	2.55	0.37	4.09E-15	3.87E-15	0.140	0.148	0.003647±0.000026	0.30	1.0057
3618-01D	XR-26	0.603	0.012	0.130	0.001	0.330	54.90	2.17	0.14	1.48E-14	8.93E-15	0.324	0.538	0.003647±0.000026	0.35	1.0057
3618-01E	XR-26	0.502	0.012	0.106	0.001	0.308	61.40	2.03	0.06	4.93E-14	2.48E-14	0.900	1.790	0.003647±0.000026	0.40	1.0057
3618-01F	XR-26	0.721	0.012	0.214	0.001	0.330	45.90	2.17	0.16	1.27E-14	9.16E-15	0.332	0.461	0.003647±0.000026	0.45	1.0057
3618-01G	XR-26	1.031	0.013	0.840	0.002	0.556	54.00	3.66	0.60	2.38E-15	2.45E-15	0.089	0.086	0.003647±0.000026	0.50	1.0057
3618-01H	XR-26	1.132	0.013	0.390	0.002	0.530	47.00	3.50	0.80	1.67E-15	1.89E-15	0.069	0.061	0.003647±0.000026	0.55	1.0057
3618-01I	XR-26	1.213	0.013	4.800	0.005	0.120	9.00	0.80	1.70	7.54E-16	9.15E-16	0.033	0.027	0.003647±0.000026	0.60	1.0057
3618-01J	XR-26	1.098	0.013	7.800	0.002	1.270	115.00	8.40	4.30	2.95E-16	3.24E-16	0.012	0.011	0.003647±0.000026	0.80	1.0057
3618-01K	XR-26	0.826	0.015	1.400	0.003	0.050	6.00	0.30	3.60	4.01E-16	3.31E-16	0.012	0.015	0.003647±0.000026	1.00	1.0057
3618-01L	XR-26	4.343	0.016	-2.50	0.017	-0.770	-18.000	-5.10	4.20	3.32E-16	1.44E-15	0.052	0.012	0.003647±0.000026	2.00	1.0057
3621-01A	XR-29	58.840	0.045	2.800	0.181	5.600	9.50	36.40	7.30	1.28E-15	7.55E-14	2.782	0.047	0.003647±0.000026	0.10	1.0053
3621-01B	XR-29	16.836	0.018	6.300	0.026	9.630	56.90	62.20	2.10	2.17E-15	3.66E-14	1.347	0.080	0.003647±0.000026	0.20	1.0053
3621-01C	XR-29	14.118	0.011	3.600	0.005	12.850	90.80	82.60	1.30	3.17E-15	4.48E-14	1.652	0.117	0.003647±0.000026	0.30	1.0053
3621-01D	XR-29	18.410	0.011	4.900	0.002	18.310	99.10	116.60	1.40	2.71E-15	5.00E-14	1.842	0.100	0.003647±0.000026	0.35	1.0053
3621-01E	XR-29	21.360	0.011	5.300	0.002	21.340	99.56	135.20	1.20	3.58E-15	7.65E-14	2.820	0.132	0.003647±0.000026	0.40	1.0053
3621-01F	XR-29	19.199	0.011	3.800	0.001	19.250	100.01	122.41	0.87	7.97E-15	1.53E-13	5.643	0.294	0.003647±0.000026	0.45	1.0053
3621-01G	XR-29	13.115	0.011	1.220	0.001	12.920	98.44	83.07	0.47	1.44E-14	1.89E-13	6.964	0.531	0.003647±0.000026	0.50	1.0053
3621-01H	XR-29	10.017	0.012	0.560	0.001	9.808	97.88	63.40	0.37	1.60E-14	1.60E-13	5.894	0.588	0.003647±0.000026	0.55	1.0053
3621-01I	XR-29	11.496	0.012	1.010	0.001	11.417	99.25	73.60	0.41	1.84E-14	2.12E-13	7.804	0.679	0.003647±0.000026	0.60	1.0053
3621-01J	XR-29	18.692	0.012	0.290	0.001	18.508	99.00	117.84	0.58	1.93E-14	3.60E-13	13.085	0.700	0.003647±0.000026	0.80	1.0053
3621-01K	XR-29	23.930	0.011	1.190	0.001	23.850	99.59	150.45	0.69	2.03E-14	4.87E-13	17.687	0.739	0.003647±0.000026	1.00	1.0053
3621-01L	XR-29	25.300	0.011	1.500	0.001	25.220	99.62	158.77	0.78	1.41E-14	3.56E-13	12.916	0.511	0.003647±0.000026	2.00	1.0053

Data were corrected for blanks, mass discrimination, nucleogenic interferences, and atmospheric contamination. Individual step apparent ages show 1σ errors

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