



Radiogenic isotope investigation of the St-Robert H5 fall

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(Received 29 June 2004; revision accepted 20 September 2004)

Abstract—The St-Robert H5 chondrite yields a mineral/whole-rock Pb-Pb age of 4565 ± 23 Ma (2σ) comparable to the accepted age of most chondrites. The regression of chondrule data give a similar age of 4566 ± 7 Ma (2σ). These results imply that no major perturbation affected the Pb-Pb systematics of this meteorite's parent body within the first few billion years following its accretion. Re and Os concentrations along with Os isotopic compositions of whole-rock fragments, surface fusion crusts and metal phases are also reported. The whole rock measurements for this ordinary chondrite are characterized by high Re/Os ratio coupled with relatively high $^{187}\text{Os}/^{188}\text{Os}$ (compared to average ordinary chondrites), that we interpret as a long term Re enrichment. As for most chondrites, no precise geochronological information could be extracted from the Re/Os systematics, although most data plot near the IIIAB reference isochron (Smoliar et al. 1996). From the fusion crust results, we rule out the possibility that atmospheric entry caused the perturbations in the Re-Os system, since melted crust analysis yields among the most concordant data points. Evidence from metal phases suggests that a very recent process perturbed the isochron, relocating Re from kamacite toward troilite.

INTRODUCTION

Chondrites are materials of foremost interest to Earth and planetary sciences. They yield abundances of nonvolatile elements comparable to that of the Sun's corona and are the oldest rocks retrieved from within the solar system. Thus, most models of primordial Earth evolution are based on geochemical and isotopic parameters derived from the study of chondrites.

Mass spectrometry developments, studies of extinct radioactivities (e.g., Wasserburg 1985), and studies of long-lived parent-daughter systems (K-Ar, Rb-Sr, Sm-Nd, Lu-Hf, Re-Os, or U-Pb) considerably refined our understanding of the early solar system's evolution (e.g., McSween 1999). Within the family of long-lived nuclides, the Re-Os system is singular: these elements are both siderophile and chalcophile and thus mainly reside in the metal and sulfide phases of meteorites.

Applications of the Re-Os system to iron meteorites, pallasites, and mesosiderites yielded important results: 1) accurate isochron ages and 2) estimates of the initial composition of the solar system (e.g., Smoliar et al. 1996; Shen et al. 1996; Birk and Allègre 1998; Chen et al. 2002). However, the initial Os isotopic composition of chondrites

and chondrite components should be lower than that of iron meteorites by a few tenths of a percent, if differentiation of the latter lasted for some 50 Ma after the parent body accretion (e.g., Allègre et al. 1995; Walker et al. 2002).

The precise Re-Os determination of chondrite formation age and initial Os isotopic composition may not be possible: these rocks likely are a mixture of cosmic grains and dust from various sources. Consequently, the criteria of uniform initial isotopic composition required to derive a valid isochron may not be fulfilled (e.g., Shirey and Walker 1998). Nevertheless, Chen et al. (1998) provided a Re-Os isochron age for the St. Séverin chondrite (LL6) that they interpreted as a melting/crystallization age. It is remarkable to see that a Re-Os isochron was obtained even though the specimen reportedly has disturbed U-Pb and Rb-Sr systematics (but Pb-Pb on phosphates is not); within the uncertainty, the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio encompassed the value determined for iron meteorites. Walker et al. (2002) analyzed a broad range of C, E, and H chondrites of different metamorphic types for their Re-Os and $^{187}\text{Os}/^{188}\text{Os}$ systematics and summarized results from previous studies. They concluded that differences in the Re/Os ratios of C versus E-H chondrites reflected chemical fractionation processes early in the history of the solar system. In addition, deviations of most chondrites from a

4.56 Ga reference isochron were attributed to post-formation redistribution of Re and/or Os. The elemental redistribution scale was of millimeters to centimeters and due to any one of the following processes: terrestrial weathering, aqueous alteration, or shock events on the parent body within the past 2 Ga (Walker et al. 2002). With the notable exceptions of Allende and St. Séverin, there are few Re-Os data for individual components of chondrites.

This paper reports Pb-Pb and Re-Os isotopic data obtained on rock fragments, fusion crusts, chondrules, and metal phase separates from a single chondrite, the St-Robert H5 fall of 1994. Our goal was two-fold: 1) assess the age, equilibrium state, and post-accretion history of St-Robert using the Pb-Pb systematics and 2) elucidate the processes responsible for the typical open-system behavior of the Re-Os system in most ordinary chondrites.

THE ST-ROBERT CHONDRITE

The St-Robert fall (45°58'N; 72°58'W) occurred on June 14, 1994 at ~60 km NE of Montreal. Studies by Wilson (1994), Brown et al. (1996), and Leya et al. (2001) have concluded that: a) it is a monomict breccia of a H5 ordinary chondrite with S2-S3 shock levels; b) it has a high porosity and a high permeability when compared to most ordinary chondrites; c) the well-preserved fusion crust is ~50% more permeable than a freshly cut surface; d) it was launched from deep in its parent body about 7–8 Ma ago and, without undergoing further major collision, entered in orbital resonance with Jupiter and then traveled to the Earth; e) the modeled orbit is consistent with an aphelion located within the asteroid belt; and f) the pre-atmospheric mass was between 1 and 2 tons at an entry velocity of ~13 km/s.

The Geological Survey of Canada organized a prompt search for fragments and recovered ~25.4 kg of materials from arable land environments. A consortium of Quebec universities acquired a series of St-Robert samples. The analyzed specimen is that of Université du Québec à Montréal (UQAM). After acquisition, the specimen was placed on a ceramic plate and stored in a glass dessicator in dry nitrogen atmosphere.

Compositionally, the St-Robert meteorite is an unremarkable object, typical of a large group of H chondrites which were produced in a major collision 7 to 8 Ma ago (Leya et al. 2001). However, it is one of a few where the simple post-collision history is well documented, the orbital parameters well established and the recovery occurred within days after the fall event.

ANALYTICAL TECHNIQUES

Using a tungsten carbide chisel, about 10 g was broken off the UQAM specimen and separated into two aliquots. An ~2.5 g bulk fragment was manually powdered in an agate

mortar and pestle apparatus and analyzed for its major and trace element contents by instrumental neutron activation at the SLOWPOKE laboratory of Ecole Polytechnique de Montréal. Isotopic analyses were performed on the second aliquot that was gently crushed between tungsten carbide plates, which were subsequently found to be a potentially problematic source of Re contamination, especially for the smallest samples. The St-Robert fall proved to be a quite fragile rock and those plates were used only for the first, rough crushing of the fragment. Before handpicking, the more delicate crushing was accomplished manually with agate mortar and pestle. Most of the chondrules and metal chunks were retrieved directly from whole rock pieces under a microscope. Whole-rock, fusion crust fragments, mineral grains, and chondrules were all handpicked. An additional "magnetic fraction" was separated using a small hand magnet covered with plastic film. It clearly contained partially rusted metal grains, demonstrating that some humidity had come into contact with the meteorite, but we cannot say much about the source of that water. (We exclude the possibility of water from the soil where the meteorite was recovered, since it would have had affected predominantly the external crust, and this is not the case: see Re-Os results below).

The composition of a few grains of each mineral and chondrule separates was assessed using a scanning electron microscope (SEM) equipped with an energy-dispersive system. All chemical treatments were carried out in HEPA class 100 laboratories using reagents systematically monitored for their Re, Os, and Pb levels.

Pb Isotope Separation

Before weighing, all solid aliquots were washed in distilled methanol and dried. They were dissolved in sealed teflon capsules using a concentrated HF-HNO₃ acid mixture, placed on a hot plate for ~1 week, and shaken daily using an ultrasonic bath. After evaporation, the salts were taken up in 0.8N HBr and centrifuged. The residues from centrifugation were systematically examined under the microscope to ensure complete digestion (although some fluoride precipitates may have remained invisible). Weighted aliquots of the solutions were spiked with a pure ²⁰⁶Pb tracer (NIST-SRM-991) and calibrated against the NIST-SRM-981 standard to obtain Pb concentrations by the isotope dilution technique. Lead was isolated from the matrix using anion exchange chromatographic techniques adapted from Manhès et al. (1980), initially using a three-pass procedure. This yielded total Pb blanks in the range of 55 ± 15 pg. This intensive purification was found to be excessive for ICP-MC-MS measurements and reduced to a two-pass procedure, bringing the blank level below 40 pg. For consistency with the actual sample measurements, the blank levels were also determined by ICP-MC-MS using the Faraday cages assembly. The measured blank level is clearly higher than that determined by

TIMS using similar preparation procedures under the same laboratory conditions (typically 10–20 pg). This can only be explained by an additional source of Pb contamination related to the use of the ICP instrument. Possible causes are: 1) the use of additional solvents and carrier gases for which we did not detect any measurable contribution, or most likely, 2) “memory effects” arising from the introduction system, the sampler cones, or the hexapole collision cell. The third possibility may reside in the difficulty to precisely measure a blank using Faraday cups. When the different sources of uncertainties are propagated, the large variance in blank levels determined by ICP is the main source of uncertainty and largely exceeds that of analytical statistics and mass fractionation corrections, especially for radiogenic samples. For error propagation calculations, Pb blank levels of 55 ± 15 pg and 40 ± 10 pg were applied depending on the separation procedure used.

Re-Os Isotope Separation

The chemical separation of Re and Os followed the protocol of Birck et al. (1998). After a HF-HBr dissolution stage at ~ 135 °C for 48 hr in tightly sealed Teflon bombs, 1 ml of concentrated HNO_3 , 0.5–1 ml of Cr^{VI} in 4N HNO_3 , and 1 ml of $\text{Br}_{2(l)}$ were added to the solution. Chromium oxide is added to ensure spike-sample equilibration by driving all the Re and Os to their highest oxidation state, while bromine is used to trap the volatile OsO_4 so formed. The osmium tetroxide is then extracted with the liquid bromine and further purified by micro-distillation. Total procedural Os blanks were always <0.3 pg and negligible. Rhenium was recovered from the remaining aqueous solution. It was first extracted into isoamyl alcohol and then in Milli-Q water. The Re blank levels averaged 30 ± 5 pg for teflon digestion and 20 pg for the Carius Tube digestion process (see below) where no CrO_3 is used. The Re blank represents less than 1% of the total Re content for most samples, with the exception of the smallest troilite and kamacite separates.

Given that potential equilibration problems were reported for digestion techniques other than the Carius Tube (CT) procedure (Shirey and Walker 1995), two rock fragments and one metal-rich piece were processed using the CT technique for comparison. A Carius Tube containing the sample, spikes, and inverse aqua regia ($3\text{HNO}_3 + 1\text{HCl}$) was sealed and slowly brought to 240 °C for at least 24 hr. After CT opening, the Os and Re recovery procedures were the same as for the HF-HBr digestion processes.

The ^{190}Os spike was gravimetrically calibrated against a solution of a K_2OsCl_6 salt obtained from Electronic Space Products International (Ashland, OR, U.S.A.) which was reported to be stoichiometric (Yin et al. 2001). The ^{185}Re spike was gravimetrically calibrated against a standard solution of a zone-refined Re ribbon obtained from Rhenium Alloys Inc. (Elyria, OH, U.S.A.), the type of material

commonly used as “filament” in TIMS. The external reproducibilities for Re and Os spike concentrations were better than 0.4% (assuming the standard concentrations as known perfectly during reversed isotope dilution).

Mass Spectrometry

Pb and Re isotope measurements were performed using a magnetic sector multicollector ICP-MS instrument (model IsoProbe from Micromass) and Faraday cup collectors with $10^{11} \Omega$ feedback resistors. The collector relative efficiencies were set to unity and amplifier gains were calibrated daily. All purified samples were dissolved in a 2% HNO_3 solution and aspirated freely through an Aridus desolvating microconcentric nebulizer and swept by the Ar carrier gas into the plasma torch. Between samples, wash solutions of 10% and 2% HNO_3 are alternatively aspirated until the background signal returns to a constant level, as measured with the same acid solvent used for sample introduction. For Pb measurements, this level corresponds to a very stable signal of a 1–2 mV on mass ^{208}Pb compared to the background noise determined with the flight tube isolation valve closed; for Re measurements, there are no detectable memory effects on Faraday cups.

The Os isotopic measurements were done by thermal ionization mass spectrometry (TIMS) using a VG Sector 54 instrument operated in negative ion mode.

Pb Isotope Measurements

The purified salts (typically 1–2 ng of Pb) were dissolved in a thallium-bearing HNO_3 2% solution. Data acquisition in static multi-collection consisted of 50×4 sec scans; the raw data were processed off-line, cycle by cycle to correct for on-peak-zero, abundance sensitivity effects (Thirlwall 2001, 2002), mass fractionation, and blank contribution. Tail corrections were based on the method proposed by Deschamps et al. (2003) for uranium (see also Doucelance et al. 2003). A power law (Russell 1978) was used for mass fractionation corrections. The $^{203}\text{Tl}/^{205}\text{Tl}$ ratio of the NIST SRM-997 standard used to correct for mass fractionation was determined empirically: its value ($^{203}\text{Tl}/^{205}\text{Tl} = 2.3899$, $n = 32$) was adjusted from repeated analyses of the NIST SRM-981 Pb standard mixed with the same $\text{HNO}_3 + \text{Tl}$ solution, over a period of several months. This value minimizes the differences in all three ^{206}Pb -normalized ratios with respect to the accepted values for the SRM-981 standard (Doucelance and Manhès 2001 in Thirlwall 2002). Repeated analysis of NBS-981 yielded: $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677 \pm 0.0002$; $^{207}\text{Pb}/^{206}\text{Pb} = 0.9149 \pm 0.0002$; $^{206}\text{Pb}/^{204}\text{Pb} = 16.9480 \pm 0.0008$. The Tl isotopic composition is comparable, within error limits, to the value of Thirlwall (2002) but 540 ppm higher than that of IUPAC.

Isotope dilution (spiked with ^{206}Pb) and isotope composition samples were grouped in different batches and

analyzed on separate analytical sessions to minimize memory effects, notably from the desolvating membrane of the nebulizer. Collerson et al. (2002) showed that up to 6% retention of the processed Pb may occur in such introduction devices, resulting in potential cross-contamination phenomena. In this study, the total amounts of Pb introduced in the instrument were always lower than 2 ng/sample, typically corresponding to an aspiration rate of 1–10 pg Pb/sec (with ~60 µl/min uptake rate). The very low Pb amounts introduced minimizes “memory effects” from the introduction system, but in first approximation does not reduce the sample-to-sample cross-contamination ratio because of the approximately similar Pb abundances. However, the in-between sample wash-out procedure (typically 20–40 min) becomes considerably more efficient in eliminating small amounts of “memory” Pb rather than very large ones.

Re Isotope Measurements

The purified Re salts were dissolved in a 2% HNO₃ solution doped with tungsten. This approach is analogous to the addition of Tl for on-line mass bias monitoring of Pb isotopic compositions by MC-ICP-MS. Tungsten has stable isotopes in the 180 to 186 mass range. It does not have any isobaric interferences with Re. We used the ratio of ¹⁸⁶W/¹⁸⁴W = 0.927633 (as determined by Lee and Halliday 1995) to correct the measured ¹⁸⁷Re/¹⁸⁵Re ratio for mass fractionation in ICP-MC-MS instrument. This approach improves the external reproducibility on standard measurements three-fold when compared to the conventional standard-sample bracketing technique (Poirier 2001). Abundance sensitivity effects are negligible on the measured Re concentrations. Mass 188 was monitored for potential Os interferences on Re and W masses.

Os Isotope Measurements

Osmium isotopic compositions and concurrent isotope dilution abundances were determined by negative-TIMS (Creaser et al. 1991; Völkening et al. 1991) using an ion source (collimator), filament block holders, cover slits, and filaments dedicated to the analysis of Os. All Os isotopic signals, but ¹⁸⁴Os, were collected as trioxides in static multi-collector mode. The oxygen bleeding rate into the source of the mass spectrometer was optimized for each sample (typical resulting pressure: 2–3 × 10⁻⁷ Torr). Faraday cup efficiencies were set up at unity and the amplifier gains monitored daily. ¹⁸⁵Re¹⁶O₃ (mass 233) was systematically monitored for potential interferences on ¹⁸⁷Os. Osmium was loaded in HBr on a zone-refined platinum filament and covered with 0.5 µl of a freshly prepared barium hydroxide solution. Isotope dilution calculations, oxide contribution, and fractionation corrections (normalized to ¹⁹²Os/¹⁸⁸Os = 3.08271; Nier 1937) were performed off-line. In-house standard repeated analysis (corrected to ¹⁹²Os/¹⁸⁸Os = 3.08271) gives ¹⁸⁶Os/¹⁸⁸Os =

0.11993 ± 0.00015; ¹⁸⁷Os/¹⁸⁸Os = 0.10704 ± 0.00012; ¹⁸⁹Os/¹⁸⁸Os = 1.21951 ± 0.00032; and ¹⁹⁰Os/¹⁸⁸Os = 1.98358 ± 0.00019.

In addition to our in-house standard measurements, analysis of an aliquot of the standard solution LOsTD were performed. This solution (provided by Thomas Meisel, University of Leoben) is now being analyzed by many laboratories as an osmium inter-laboratory mass spectrometry standard. We obtained ¹⁸⁷Os/¹⁸⁸Os = 0.10689 ± 5, (1σ, n = 5). This value is within error to the mean of all analyses reported by 14 different labs (T. Meisel, personal communication).

RESULTS

Elemental Concentrations

Table 1 shows Instrumental Neutron Activation Analysis (INAA) results for major and trace elements in a whole-rock aliquot of St-Robert. When compared to other H chondrites, this meteorite has similar abundance patterns for both lithophile and siderophile/chalcophile elements (Horan et al. 2003).

Lead Isotopes

The total Pb abundances and the isotopic data for 17 sub-samples of St-Robert are listed in Table 2. The concentrations range from 4 to 290 ppb and the ²⁰⁶Pb/²⁰⁴Pb ratios vary by an order of magnitude (17–300) when the acid-washed chondrules are taken into account. The 3 WR fragments and the 2 fusion crusts have ²⁰⁴Pb concentrations (non-radiogenic Pb) in the range of 0.07–0.13 ppb, averaging 0.1 ppb. Assuming that these are representative of the entire rock, the initial Pb content of St-Robert is on the same order as the lowest values reported in the literature for H chondrites (e.g., Wasson and Kallemeyn 1988; Göpel et al. 1994). Thus, this sample would be very sensitive to crustal contamination, but shows no evidence for it.

Table 1. Whole-rock elemental abundances.

	wt%		ppm
Fe	25.0	Sc	7.9
Si	18.4	As	1.8
Mg	13.7	Se	10.6
Ni	1.51	Sb	0.04
Ca	1.22	La	0.30
Al	1.01	Sm	0.19
Na	0.62	Eu	0.09
Cr	0.35	Yb	0.21
Mn	0.24	Re ^a	0.08
	(ppm)	Os ^a	0.84
K	724	Ir	0.69
Co	726	Au	0.19
V	73		

^aMean of 10 WR analyses by isotope dilution.

Table 2. Pb isotopic results, fractionation and blank corrected, with their propagated errors at the 95% level of confidence.

Sample	Weight (g)	Pb (ppb)	$^{206}\text{Pb}/^{204}\text{Pb}$ ($\pm 2\sigma$)	$^{207}\text{Pb}/^{204}\text{Pb}$ ($\pm 2\sigma$)	$^{208}\text{Pb}/^{204}\text{Pb}$ ($\pm 2\sigma$)
WR fragment 1	0.12922	12.89	29.960 ± 0.173	23.321 ± 0.115	48.777 ± 0.153
WR fragment 2	0.13091	7.84	32.402 ± 0.405	24.825 ± 0.266	49.993 ± 0.331
WR fragment 3	0.13364	7.88	30.317 ± 0.322	23.565 ± 0.215	48.390 ± 0.266
Fusion crust 1	0.20116	8.17	20.052 ± 0.022	16.796 ± 0.015	39.557 ± 0.014
Fusion crust 2	0.13586	8.13	20.450 ± 0.042	17.084 ± 0.030	39.640 ± 0.023
Troilite	0.00994	197.71	16.891 ± 0.011	15.051 ± 0.015	37.008 ± 0.012
Kamacite 1	0.11701	14.39	18.448 ± 0.012	15.789 ± 0.010	38.301 ± 0.012
Kamacite 2	0.20433	7.08	18.989 ± 0.010	16.278 ± 0.010	39.186 ± 0.010
Magn. fraction	0.26256	4.13	19.927 ± 0.034	16.780 ± 0.025	39.180 ± 0.015
Grey pyroxene 1	0.03683	45.34	82.272 ± 2.189	55.726 ± 1.374	82.245 ± 1.498
Pale pyroxene 2	0.00551	290.55	40.556 ± 0.465	29.528 ± 0.292	56.786 ± 0.383
Chondrule 1	0.01835	96.30	50.175 ± 0.717	35.462 ± 0.448	69.005 ± 0.687
Chondrule 2	0.03931	40.92	85.323 ± 2.588	57.416 ± 1.616	89.094 ± 1.955
Chondrule 3	0.02212	65.47	72.577 ± 2.129	49.604 ± 1.335	85.927 ± 1.861
Chondrule 4 ^a	0.02310	64.19	301.585 ± 23.85	192.217 ± 14.87	279.208 ± 20.26
Chondrule 5 ^a	0.01140	126.74	198.839 ± 30.56	128.704 ± 19.15	206.559 ± 28.45
Chondrule 6 ^a	0.02300	58.91	102.339 ± 7.421	68.306 ± 4.658	115.686 ± 6.817

Sample	$^{207}\text{Pb}/^{206}\text{Pb}$ ($\pm 2\sigma$)	Error correlations		$^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ($\pm 2\sigma$)	Model age (Ma)
		$^{204}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$		
WR fragment 1	0.7784 ± 0.0008	0.890	0.996	0.6308 ± 0.0006	4581 ± 1
WR fragment 2	0.7661 ± 0.0016	0.892	0.996	0.6292 ± 0.0011	4577 ± 3
WR fragment 3	0.7773 ± 0.0014	0.891	0.996	0.6317 ± 0.0010	4583 ± 2
Fusion crust 1	0.8376 ± 0.0002	0.893	0.995	0.6051 ± 0.0002	4520 ± 1
Fusion crust 2	0.8354 ± 0.0003	0.892	0.995	0.6094 ± 0.0004	4530 ± 1
Troilite	0.8911 ± 0.0004	-0.589	0.927	0.6273 ± 0.0012	4572 ± 3
Kamacite 1	0.8559 ± 0.0001	0.334	0.996	0.6011 ± 0.0003	4511 ± 1
Kamacite 2	0.8572 ± 0.0001	-0.849	0.997	0.6180 ± 0.0004	4551 ± 1
Magn. fraction	0.8421 ± 0.0002	0.887	0.997	0.6107 ± 0.0004	4534 ± 1
Grey pyroxene 1	0.6773 ± 0.0015	0.884	0.999	0.6227 ± 0.0008	4562 ± 2
Pale pyroxene 2	0.7281 ± 0.0013	0.890	0.997	0.6155 ± 0.0008	4545 ± 2
Chondrule 1	0.7068 ± 0.0014	0.888	0.998	0.6158 ± 0.0008	4546 ± 2
Chondrule 2	0.6729 ± 0.0017	0.885	0.999	0.6199 ± 0.0009	4555 ± 2
Chondrule 3	0.6835 ± 0.0019	0.886	0.999	0.6213 ± 0.0010	4559 ± 2
Chondrule 4 ^a	0.6374 ± 0.0012	0.884	0.999	0.6224 ± 0.0006	4561 ± 1
Chondrule 5 ^a	0.6473 ± 0.0034	0.926	0.999	0.6248 ± 0.0014	4537 ± 3
Chondrule 6 ^a	0.6675 ± 0.0033	0.894	0.999	0.6236 ± 0.0016	4564 ± 4

^aSequential leaching with 0.2N, 3N, and 6N HCl. Blank composition is $^{204}\text{Pb} : ^{206}\text{Pb} : ^{207}\text{Pb} : ^{208}\text{Pb} = 1 : 18.20 : 15.50 : 38.40$.

Figure 1 illustrates the variations in $^{206}\text{Pb}/^{204}\text{Pb}$ as a function of the initial Pb content of the sub-samples. The data define two broad arrays. A sub-horizontal array comprises the metal phases, the magnetic fraction and the fusion crusts with a limited spread of $^{206}\text{Pb}/^{204}\text{Pb}$ values (16.9–20.5): the magnetic fraction is the poorest in ^{204}Pb and troilite the richest. For comparable ^{204}Pb levels, the WR fragments yielded higher $^{206}\text{Pb}/^{204}\text{Pb}$ ratios (30.0–32.4). The pyroxene and chondrule fractions yielded the most radiogenic compositions and define a steep array on Fig. 1. Note that the ^{204}Pb concentrations of the acid-leached chondrules are relative to the total weights before washing; thus, their true position on Fig. 1 are left of that illustrated, depending on the

amount of Pb removed by the acid treatment (leaches' measured $^{206}\text{Pb}/^{204}\text{Pb}$ were between 16.1–16.9). The radiogenic signatures of the Pb in silicate fractions are clearly related to their content in non-radiogenic ^{204}Pb . Thus, the steep array on Fig. 1 likely represents mixing in different proportions, between a radiogenic end-member and unradiogenic component(s) represented by matrix phases such as troilite or troilite $\pm$ metals.

Pb-Pb Isochron Ages

Figure 2 shows Pb-Pb isochron diagrams for different sample subsets. The statistical treatments were done with the

Isoplot 2.49 software of Ludwig (2001) and all errors are quoted at the $\pm 95\%$ confidence level. All values refer to the “model 1 solution” calculation where the analytical errors are the only reason for data point scatter along a straight line. The choice of Isoplot model calculation will affect the uncertainty of the age, but not the MSWD (mean square of weighted deviates). The first model was chosen for all calculations to simplify comparison of all the computed ages.

The regression results for all 17 sub-samples are shown on Fig. 2a using data corrected for mass fractionation, blank contribution, and their propagated uncertainties. It yields an age of 4567 ± 23 Ma with a MSWD value of 789. This large scatter indicates that the analyzed fractions: 1) did not form at the same time and/or same initial Pb isotopic composition. For example, Amelin et al. (2002) reported Pb-Pb ages for calcium-aluminium inclusions (CAI) of CV chondrites which are some 2–3 Ma older than that of CR chondrules. Alternatively, Itoh and Yurimoto (2003) found chondrule fragment embedded in a CAI, indicating a synchronous formation for both components; and/or 2) were perturbed by secondary phenomena (i.e., shock metamorphism, aqueous alteration, etc.).

Figure 2b shows the regression results for the six chondrule fractions. The derived age is 4566 ± 7 Ma, with a MSWD value of 12 and a null probability of fit (Ludwig 2003). Regression of the pyroxene data with the chondrules (not illustrated) does not significantly change these results, suggesting that the pyroxene mineral separates actually are chondrule fragments. Regression of the three acid-washed, and most radiogenic chondrules alone yields an age of 4560 ± 46 Ma (MSWD = 7).

Pb-Pb model ages are calculated assuming that the initial lead value was that of the Canyon Diablo troilite (CDT, Tatsumoto et al. 1973). By subtracting this primordial lead from the actual sample composition, we get the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio, which has age significance. Model age results from the calculations with CDT initial lead are shown in Table 2. Leached chondrules converge to a value of ~ 4564 Ma at high $^{206}\text{Pb}/^{204}\text{Pb}$, while unleached fractions give lower values indicative of unradiogenic Pb from the matrix adhering on their surfaces. Previous studies have demonstrated a tendency for more radiogenic phases to give “correct” Pb-Pb age (e.g., Allègre et al. 1995); this may be rationalized by the fact that these phases contain more Pb that is related to the duration of U-decay (less sensitive to initial lead composition). The whole rocks yield ages up to 4580 Ma, which are higher than the chondrule results. This can be explained by radiogenic terrestrial contamination of the unleached whole rock.

Although the fit of the regression line to the data is far from perfect, we conclude from the Pb-Pb result on chondrules that no major perturbation affected this meteorite in the first few billion years of its existence (a very recent thermal event would not be detected from Pb-Pb systematics).

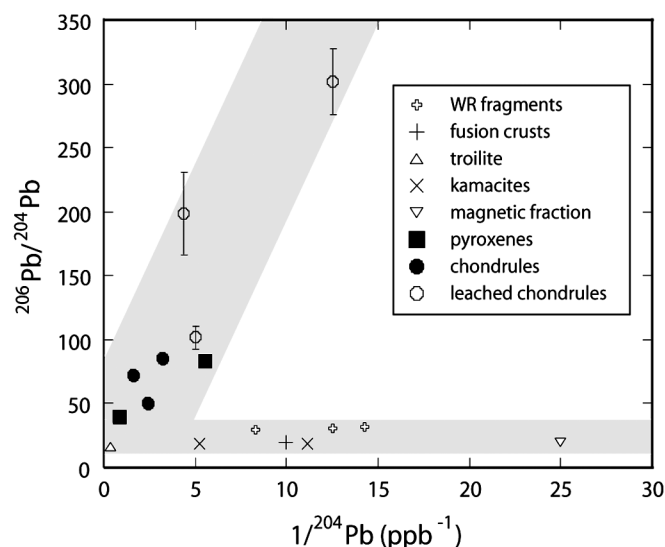


Fig. 1. $1/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram indicating two main trends for the data set: The first one controlled by U decay, and another by common (initial) lead content.

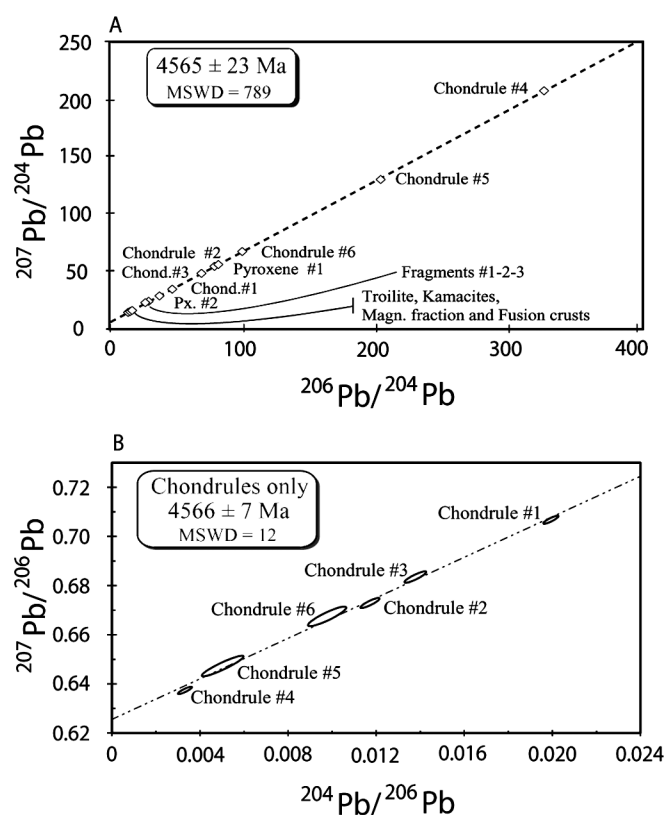


Fig. 2. Pb-Pb isotope results for St-Robert H5 chondrite presented in isochron diagrams. Errors are given at 2σ confidence interval. Data points are blank and fractionation corrected; a) internal Pb-Pb isochron (see Table 2 for data). Comprised in the error envelope of the regression is the primordial lead value from Tatsumoto et al. (1973) with $^{207}\text{Pb}/^{204}\text{Pb} = 9.307$ and $^{206}\text{Pb}/^{204}\text{Pb} = 10.294$; b) diagram of $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ for the chondrule separates only. Ages computed with Isoplot/Ex 2.49 (Ludwig 2001).

Re-Os Systematics

The Re-Os systematics of chondrite bulk samples and components are difficult to interpret. Replicate analysis of whole rocks show significant scatter relative to a 4.56 Ga reference isochron, the assumed age of formation. The reason for such dispersion of chondrite data remains unclear. Recent perturbation of Re has been previously invoked for other chondrite, but the exact cause is still uncertain (Walker et al. 2002; Horan et al. 2003). We examined 10 pieces of St-Robert whole-rock and several separated metal-rich components. We also analyzed the fusion crust. This was done to investigate the possible influence of atmospheric entry fusion on the Re-Os system.

Whole Rocks

The St-Robert mean Re and Os concentrations calculated from 10 whole-rock fragments are of 82 ± 11 ppb and 841 ± 122 ppb (1 σ), respectively, and fall within the array defined by most ordinary chondrites (Chen et al. 1998; Walker et al. 2002). The >40% range ([maximum-minimum]/mean) of the Os and Re concentrations of replicate analysis suggests a strong control by the heterogeneously distributed FeNi alloy for both elements. The ranges obtained here are wider than that reported by Horan et al. (2003). The difference may be due to the larger data set and greater odds to sample different metal contents among powder splits. The range in Re/Os ratio of the St-Robert fall is also wide (27% controlled by WR-7; 16% when excluding it). Such results show more variability than ordinary chondrites values of Horan et al. (2003). The ratio of these elements is likely unrelated to the amount of metal sampled in each split (the carrier phases for both Re and Os). This implies either that some disturbance may have variably affected this H5 specimen, or that some technical problem occurred. The Carius Tube technique used by Walker et al. (2002) was used on 2 splits of whole rock powder of the St-Robert specimen. These show the same large range of concentrations and Re/Os ratio (deviation of: 16% for [Os], 30% for [Re] and 14% for Re/Os). This confirms that the observed variability in the Re/Os in this specimen is real and that HF-HBr digestion yields results as reliable as CT digestion for ordinary chondrites. High variability in both Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ was also found for constituents of Tieschitz chondrite by Smoliar et al. (2004), who showed significant fractionation of Re from Os in some components of ordinary chondrites.

The fact that the $^{187}\text{Os}/^{188}\text{Os}$ shows a more narrow range of values (5%) indicates that a Re/Os ratio perturbation occurred fairly late in the history of the meteorite. On the other hand, the mean $^{187}\text{Re}/^{188}\text{Os}$ of 0.4690 is 11% higher than the mean ordinary chondrites (OC) value of Walker et al. (2002). The corresponding mean $^{187}\text{Os}/^{188}\text{Os}$ being also higher than average OC (1.4% higher) leads us to conclude that the Re enrichment (or Os loss) is due to a long term event.

This requires multiple stages of open-system behavior. Firstly, an early Re/Os fractionation resulted in a higher original bulk rock elemental ratio; secondly, a more recent process is needed to explain the scattering observed in the present-day Re/Os ratio (and Os isotope signature).

When plotted on an isochron diagram (Fig. 3), most WR data points scatter along the IIIAB regression line (4558 Ma, Smoliar et al. 1996). This indicates that the high Re/Os ratio relative to the OC average was most likely acquired very early in the chondrite's history, perhaps during the first 50 Ma (Walker et al. 2002) giving enough time for ^{187}Re to decay and yield the observed high $^{187}\text{Os}/^{188}\text{Os}$. Mechanisms for the early fractionation of Re from Os extend from high-temperature nebular condensation phenomenon to low-temperature fluid transport during grade 5 metamorphism on the parent body. Determining which one applied here is not possible on the sole basis of Re-Os data because both mechanisms have the same effect. The second event (or series of events) causing the Re/Os scattering is more puzzling. It might in part be related to the shock metamorphism (S2-3 level), though Walker et al. (2002) showed that such events have limited impact. Alteration in Earth's oxidizing atmosphere (post-fall alteration) was invoked by most previous studies to rationalize some of the dispersal of Re-Os data. We agree with this hypothesis because Re is very mobile in Earth's surface conditions.

On Fig. 3, we observe that most of our data plot on the high-Re side of the IIIAB reference isochron; 70% of the whole rock analyses ($n = 10$) fall on the Re-rich side of the iron meteorites reference isochron in this study. A similar

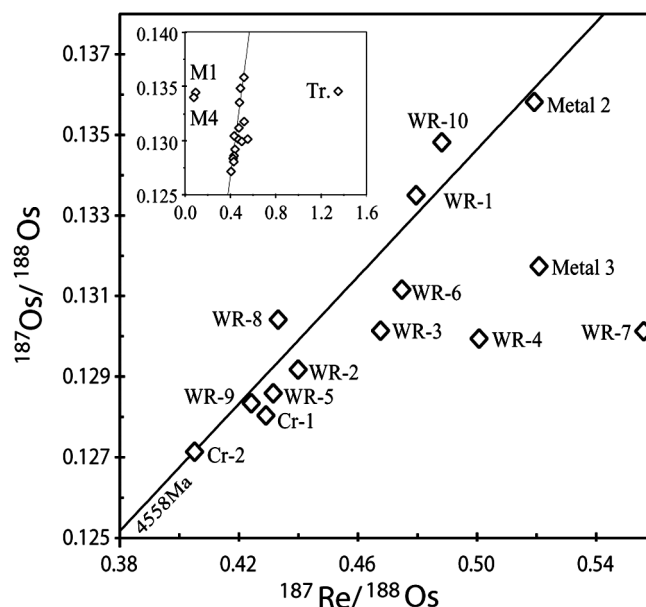


Fig. 3. Re-Os data shown in an isochron diagram. The 4558 Ma line is a reference isochron from the IIIAB iron meteorite (Smoliar et al. 1996). WR = "whole rock" fragment; Tr = troilite pure separate; M = metal-rich fragment; Cr = fusion crust.

observation was made in previous studies (Walker et al. (2002): 58%, $n = 34$ ordinary chondrites; Chen et al. (1998): 75%, $n = 12$ H chondrites). From the two most discordant WR data points (WR-4 and -7) and the extremely discordant troilite value, we calculated a secondary isochron age of 248 ± 26 Ma (MSWD = 0.69) which may point to some spatially restricted elemental exchange at that time, perhaps along a fracture.

When theoretical Re/Os is calculated from the $^{187}\text{Os}/^{188}\text{Os}$ to stay clear of a recent elemental mobilization effect as in Walker et al. (2002) study, we obtain Re/Os mean value of 0.0911 ± 0.0050 (1σ), which is slightly higher than (but overlaps within uncertainty) the 0.0876 ± 0.0052 (1σ) given by Walker et al. (2002). This gives further support to the hypothesis of recent elemental perturbation at the whole rock level of the St-Robert meteorite.

As the host phase for PGE-rich opaque assemblages, calcium-aluminium-rich inclusions (CAI) have an important role in the Re-Os budget (Blum et al. 1988). Although some occurrences were reported, their modal abundance in ordinary chondrites is very low. This may contribute to some of the observed scatter since both dissolution techniques employed here may not completely digest CAIs. Moreover, a recent study from Meisel et al. (2003) suggests that the HF-HBr dissolution and CT procedures are both ineffective for digesting Os of some specific mineral phases of serpentinized peridotite such as spinel. Their results indicate that the HF-HBr has a lower Os yield than CT which also has a low yield when compared to high pressure asher attacks. Our results do not support such claim for ordinary chondrites—the Os concentrations and Re/Os ratios obtained from CT attacks being indistinguishable from the HF-HBr attacks. Nevertheless, it remains possible that some refractory Re-Os carrying phases were not effectively digested by either technique (although these phases would probably be insensitive to mild secondary effects which would affect sulfides).

Fusion Crusts

Fusion crusts represent the remainder of the surface melt that occurred during the incandescent stage of meteoroid fall (due to atmospheric drag). Following the fireball is the dark flight during which the last fused material cools off and the hot surrounding atmosphere oxidizes elemental iron contained within this melt to produce magnetite. This process creates the characteristic black crust that is often seen on Fe-rich meteorites. This rapid high-temperature oxidation could affect rhenium and osmium concentrations: the volatile nature of these two elements, when in oxide form, might favor a loss. Moreover, the high permeability of this crust (Leya et al. 2001) might facilitate mobility of gases within it (both osmium and rhenium form volatile oxides at high $f\text{O}_2$). The analysis of two fusion crusts gave results quite comparable to the WR data in Re and Os abundances and Re/Os ratio. They gave low $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ values but are among

the closest to the IIIAB isochron data; in fact Cr-2 is the most concordant datum (-0.5 delta unit, see Table 3). These results suggest that the surface's extensive melting/volatilization during the atmospheric entry—a dramatic phenomenon for a meteorite does not affect significantly the Re-Os systematics.

Let us consider in more detail what effect the melting process may have on the crust's Re/Os system. By melting, the region is homogenized for both $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ ratios, cancelling any small scale Re/Os differences between mineral phases involved in the melt (with no major Re/Os partitioning in the resulting glassy crust). This should not necessarily render the whole crust homogeneous because of the initial Re/Os variations throughout the meteorite and since only negligible lateral mixing of melt occurs all along the meteorite's surface (as seen from the heterogeneous $^{187}\text{Os}/^{188}\text{Os}$ and Re/Os of our two analyzed crusts). Heterogeneities will be attenuated by the melting event, and if the phases involved were originally on both sides of the isochron, a resulting mixture of the right proportion could fortuitously be located right on the 4.56-Ga isochron. Hence, less scatter around the isochron can be expected for fusion crusts, just as our limited data set shows. Sampling of larger mass of crust could also help minimize the scatter even more. However, despite an acceptable age value (i.e., close to 4.56 Ga) and a better MSWD of such crusts being computed by regression, this would represent only a somewhat spurious correlation.

Metal Phases

Kamacite-rich grains were sampled along with many small troilite pieces. Pure troilite (FeS) can be sub-sampled because its brittleness helps its breaking loose from the surrounding silicate, although in very small pieces. In contrast, kamacite is ductile and does not separate easily from silicate minerals. The $^{187}\text{Re}/^{188}\text{Os}$ ratio measured in St-Robert pure sulfide is much higher than any WR results. As in the case of the sulfide phase from St. Séverin (Chen et al. 1998), the St-Robert sulfide has a disturbed Re-Os systematics and gives a model age of 1.7 Ga. When considered alone, the sulfide might be indicative of the late-stage shock that imparted the S2-S3 level of this meteorite, although we wish to issue a caveat about this datum because of its low Re sample to blank ratio (almost 2:1). The Re and Os concentrations of kamacite-rich fragments are anti-correlated to their silicate content (the smaller piece was pure kamacite), indicating dilution of the siderophile elements by low-HSE silicate phases. The very low $^{187}\text{Re}/^{188}\text{Os}$ of 2 kamacite-rich fragments indicate a strong disturbance of the rhenium-osmium distributions (Re loss and/or Os uptake). This disturbance must have occurred recently since the $^{187}\text{Os}/^{188}\text{Os}$ of the perturbed fragments are close to average WR.

Although some Re contamination coming from tungsten carbide plates is not possible to rule out for the troilite data (nor for any other sample), we believe it is very minor. Otherwise, the small metal-4 (2.4 mg) would have been

Table 3. Re-Os isotopic results, fractionation and blank corrected.

Sample	Weight (g)	Re (ppb)	Os (ppb)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os} (\pm 2\sigma)^a$	Delta
WR 1	0.0522	81.25	817.1	0.47950	0.13350 ± 3	4.5
WR 2	0.0847	67.40	738.4	0.43986	0.12918 ± 2	-7.6
WR 3	0.0534	76.25	786.0	0.46757	0.13014 ± 2	-19.7
WR 4	0.0484	82.94	800.2	0.49954	0.12991 ± 1	-47.3
WR 5	0.0670	74.07	827.2	0.43150	0.12859 ± 1	-6.8
WR 6	0.0544	75.84	770.0	0.47474	0.13116 ± 1	-15.2
WR 7	0.0677	82.86	723.2	0.55227	0.13012 ± 2	-86.7
WR 8	0.0897	100.6	1119.5	0.43314	0.13041 ± 2	10.1
WR 9 CT	0.0729	73.94	840.1	0.42411	0.12834 ± 7	-3.5
WR 10 CT	0.0540	99.94	987.4	0.48814	0.13481 ± 1	10.7
Troilite	0.00187	22.63	81.0	1.35040	0.1345 ± 27	-672.1
Fusion crust 1	0.0366	76.21	855.9	0.42903	0.12804 ± 3	-10.4
Fusion crust 2	0.0231	69.39	825.4	0.40506	0.12714 ± 2	-0.5
Metal 1	0.1212	1.91	99.3	0.09277	0.13442 ± 12	318.7
Metal 2	0.0559	38.15	354.4	0.51918	0.13581 ± 30	-3.8
Metal 3 CT	0.0076	74.42	688.9	0.52079	0.13174 ± 4	-45.8
Metal 4	0.0024	56.14	3519.3	0.07691	0.13397 ± 25	326.6

^aError bars refer to the last significant digits. WR = whole rock; CT = carius tube digestion; Delta = $10000 \times (^{187}\text{Os}/^{188}\text{Os}_{\text{sample}} - [0.09524 + 0.07887 \cdot ^{187}\text{Re}/^{188}\text{Os}_{\text{sample}}])$ (Walker et al. 2002).

contaminated too, and hence would be on the high-Re side of the isochron.

One possibility to link the observations from metal phases with troilite is by electrolytic transport (Birck et al. 1998) of some of the Re from kamacite closely followed by troilite uptake due to its chalcophile nature. An isochron with a slope of near zero can be fitted through these disturbed metals indicating the very recent nature of this transport. At standard Earth's surface conditions, Re is more easily mobilized than Os (Jaffe et al. 2002; Palme, 1988 in Walker et al. 2002). If we assume that those metal phases started on the IIIAB isochron and that Os was not mobilized, then the kamacite-rich fragments lost about 700–1000 pg of Re, while troilite gained 27 pg of Re to reach its present position. Moreover, Os being an order of magnitude more concentrated than Re in those samples, it might be buffered against such elemental exchange. The fact that whole rock fragments and one metal-rich piece are not as disturbed indicates that the remobilization acted locally and might have followed only some fractures (St-Robert is a monogenic breccia).

Another possibility to explain the metal results also involves fracture. This other explanation is impact-induced partial melting of the FeNi-FeS system during the collision that liberated the meteorite from its parent body some 7–8 Ma ago (Leya et al. 2001). With regard to this question, Wilson (1994) reported metal-sulfide relations seen in thin sections of St-Robert that are consistent with a weak level shock (St-Robert is a S2-S3 shock level).

CONCLUSIONS

Pb-Pb results yielded a regression corresponding to an age of 4565 ± 23 Ma, while chondrule separates regression

corresponds to an age of 4566 ± 7 Ma (2σ). These ages agree with the accepted age of chondrite formation. This indicates that no major perturbation occurred in the early history of the parent body. As for most ordinary chondrites, the St-Robert H5 whole-rock data do not form a statistically significant Re-Os internal isochron, although they scatter around the IIIAB reference isochron. As mentioned by Walker et al. (2002), there are few explanations for such perturbed array: heterogeneous initial isotopic composition, and/or analytical problems, and/or elemental remobilization. The analytical bias was investigated: the Birck et al. (1997) technique did not give Os yields 25% lower than from Carius tube analysis, as implied by the Meisel et al. (2003) study. Nonetheless, we do acknowledge that both these techniques recently raised some suspicions (Meisel et al. 2003). Apart from analytical bias which cannot be totally excluded (including Re contamination), some of the scatter seen on the isochron diagram for the St-Robert H5 can be interpreted as the outcome of recent elemental mobilization for the most discordant data points superposed to smaller original heterogeneities not obliterated by grade 5 metamorphism. Metal phases point toward a recent event as the slope of the fit to the most perturbed data points is close to zero. This event is possibly the 7–8 Ma impact on the H parent body. Fusion crust results show that atmospheric entry did not affect differentially Re and Os. The INAA study points out that the chemistry of major and trace elements of the St-Robert meteorite is quite typical for a H5 ordinary chondrite.

Acknowledgments—This paper is dedicated to the memory of Clément Gariépy who regrettably passed away during the writing of this manuscript. G. Kennedy from Ecole Polytechnique de Montréal is thanked for INAA data. R.

Mineau (UQAM) is acknowledged for the SEM analysis. A. Poirier acknowledges scholarship grants from NATEQ and NSERC. R. Doucelance acknowledges partial PDF support through the Lavoisier grant. J. David (MRNQ) is thanked for his help during the preliminary tests that triggered this project. A. Poirier and R. Doucelance are grateful to J. C. Mareschal and P. Schiano for careful reading and comment on the manuscript. This manuscript greatly benefited from the thorough reviews of R. J. Walker, T. Meisel, and an anonymous reviewer.

Editorial Handling—Dr. Timothy Swindle

REFERENCES

- Allègre C. J., Manhès G., and Göpel C. 1995. The age of the Earth. *Geochimica et Cosmochimica Acta* 59:1445–1456.
- Amelin Y., Krot A. N., Hutcheon I. D., and Ulyanov A. A. 2002. Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. *Science* 297:1678–1683.
- Anders E. and Grevesse N. 1989. Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta* 53:197–214.
- Birck J. L. and Allegre C. J. 1998. Rhenium-187-osmium-187 in iron meteorites and the strange origin of the Kodaikanal meteorite. *Meteoritics & Planetary Science* 33:647–653.
- Birck J. L., Roy-Barman M., and Capmas F. 1997. Re-Os isotopic measurements at the femtomole level in natural samples. *Geostandards Newsletter* 20:19–27.
- Blum J. D., Wasserberg G. J., Hutcheon I. D., Beckett J. R., and Stolper E. M. 1988. “Domestic” origin of opaque assemblages in refractory inclusions in meteorites. *Nature* 331:405–409.
- Brown P., Hildebrand A. R., Green-Daniel W. E., Page D., Jacobs C., Revelle D., Tagliaferri E., Wacker J., and Wetmiller B. 1996. The fall of the St-Robert meteorite. *Meteoritics & Planetary Science* 31:502–517.
- Chen J. H., Papanastassiou D. A., and Wasserburg G. J. 1998. Re-Os systematics in chondrites and the fractionation of the platinum group elements in the early solar system. *Geochimica et Cosmochimica Acta* 62:3379–3392.
- Chen J. H., Papanastassiou D. A., and Wasserburg G. J. 2002. Re-Os and Pd-Ag systematics in group IIIAB irons and in pallasites. *Geochimica et Cosmochimica Acta* 66:3793–3810.
- Collerson K. D., Kamber B. S., and Schoenberg R. 2002. Applications of accurate, high-precision Pb isotope ratio measurement by multi-collector ICP-MS. *Chemical Geology* 188:65–83.
- Creaser R. A., Papanastassiou D. A., and Wasserburg G. J. 1991. Negative thermal ion mass spectrometry of osmium, rhenium, and iridium. *Geochimica et Cosmochimica Acta* 55:397–401.
- Deschamps P., Doucelance R., Ghaleb B., and Michelot J. L. 2003. Further investigations on optimized tall correction and high-precision measurement of uranium isotopic ratios using multi-collector ICP-MS. *Chemical Geology* 201:141–160.
- Doucelance R. and Manhès G. 2001. Reevaluation of precise lead isotope measurements by thermal ionization mass spectrometry: Comparison with determinations by plasma source mass spectrometry. *Chemical Geology* 176:361–377.
- Doucelance R., Escrig S., Moreira M., Gariépy C., and Kurz M. D. 2003. Pb-Sr-He isotope and trace element geochemistry of the Cape Verde archipelago. *Geochimica et Cosmochimica Acta* 67:3717–3733.
- Göpel C., Manhès G., and Allègre C. J. 1994. U-Pb systematics of phosphates from equilibrated ordinary chondrites. *Earth and Planetary Science Letters* 121:153–171.
- Horan M. F., Walker R. J., Morgan J. W., Grossman J. N., and Rubin A. E. 2003. Highly siderophile elements in chondrites. *Chemical Geology* 196:5–20.
- Itoh S. and Yurimoto H. 2003. Contemporaneous formation of chondrules and refractory inclusions in the early solar system. *Nature* 423:728–731.
- Jaffe L. A., Peucker-Ehrenbrink B., and Petsch S. T. 2002. Mobility of rhenium, platinum group elements, and organic carbon during black shale weathering. *Earth and Planetary Science Letters* 198:339–353.
- Kallemeyn G. W., Rubin A. E., Wang D., and Wasson J. T. 1989. Ordinary chondrites: Bulk compositions, classification, lithophile-element fractionations, and composition-petrographic type relationships. *Geochimica et Cosmochimica Acta* 53:2747–2767.
- Leya I., Wieler R., Aggrey K., Herzog G. F., Schnabel C., Metzler K., Hildebrand A. R., Bouchard M., Jull A. J. T., Andrews H. R., Wang M. S., Ferko T. E., Lipschutz M. E., Wacker J. F., Neumann S., and Michel R. 1996. Exposure history of the St-Robert (H5) fall. *Meteoritics & Planetary Science* 36:1479–1494.
- Ludwig K. R. 2001. *Isoplot/Ex 2.49, A geochronological toolkit for Microsoft Excel*. Special Publication 1a. Berkeley: Berkeley Geochronology Center.
- Lee D. C. and Halliday A. N. 1995. Precise determination of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP magnetic sector multiple collector mass spectrometry. *International Journal Mass Spectrometry and Ion Processes* 146/147:35–46.
- Manhès G., Allègre C. J., Dupré B., and Hamelin B. 1980. Lead isotope study of basic ultra basic layered complexes: Speculation about the age of the Earth and primitive mantle characteristics. *Earth and Planetary Science Letters* 47:370–382.
- McSween H. Y., Jr. 1999. *Meteorites and their parent planets*, 2nd ed. New York: Cambridge University Press. 322 p.
- Meisel T., Reisberg L., Moser J., Carignan J., Melcher F., and Brueggemann G. 2003. Re-Os systematics of UB-N, a serpentinized peridotite reference material. *Chemical Geology* 201:161–179.
- Nier A. O. 1937. The isotopic constitution of osmium. *Physical Review* 52:885.
- Palme H. and Jones A. 2003. Solar system abundances of the elements. In *Meteorites, comets, and planets*, edited by Davis A. M. Oxford: Elsevier-Pergamon. pp. 41–61.
- Poirier A. 2001. Online rhenium fractionation correction using tungsten-doping technique on a magnetic sector ICP-MS (abstract V22A-1007). 2001 AGU Fall Meeting. *Eos Transactions* 82(47).
- Russell A. D., Papanastassiou D. A., and Tomborello T. A. 1978. Ca isotope fractionation on the Earth and other solar system materials. *Geochimica et Cosmochimica Acta* 42:1075–1090.
- Shen J. J., Papanastassiou D. A., and Wasserburg G. J. 1996. Precise Re-Os determinations and systematics of iron meteorites. *Geochimica et Cosmochimica Acta* 60:2887–2900.
- Shirey S. B. and Walker R. J. 1995. Carius tube digestion for low-blank rhenium-osmium analysis. *Analytical Chemistry* 67:2136–2141.
- Shirey S. B. and Walker R. J. 1998. The Re-Os isotope system in cosmochemistry and high-temperature geochemistry. *Annual Review of Earth and Planetary Sciences* 26:423–500.
- Smoliar M., Walker R. J., and Morgan J. W. 1996. Re-Os ages of group IIA, IIIA, IVA, and IVB iron meteorites. *Science* 271:1099–1102.

- Smoliar M. I., Horan M. F., Alexander C. M. O'D., and Walker R. J. 2004. Re-Os systematics and HSE distribution in Tieschitz (H3.6): Two isochrons for one meteorite (abstract #1333). 35th Lunar and Planetary Science Conference. CD-ROM.
- Tatsumoto M., Knight R. J., and Allègre C. J. 1973. Time differences in the formation of meteorites as determined from the ratio of lead-207 to lead-206. *Science* 180:1279–1283.
- Tera F. and Carlson R. W. 1999. Assessment of the Pb-Pb and U-Pb chronometry of the early solar system. *Geochimica et Cosmochimica Acta* 63:1877–1889.
- Thirlwall M. F. 2001. Inappropriate tail corrections can cause large inaccuracy in isotope ratio determination by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry* 16:1121–1125.
- Thirlwall M. F. 2002. Multicollector ICP-MS analysis of Pb isotopes using a ^{207}Pb - ^{204}Pb double spike demonstrates up to 400 ppm/amu systematic errors in TI-normalization. *Chemical Geology* 184:255–279.
- Völkening J., Walczyk T., and Heumann K. G. 1991. Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *International Journal of Mass Spectrometry and Ion Physics* 105:147–159.
- Walker R. J., Horan M. F., Morgan J. W., Becker H., Grossman J. N., and Rubin A. E. 2002. Comparative Re-187-Os-187 systematics of chondrites: Implications regarding early solar system processes. *Geochimica et Cosmochimica Acta* 66:4187–4201.
- Wasserburg G. J. 1985. Short-lived nuclei in the early solar-system. In *Protostars and Planets II*, edited by Black D. C. and Matthews M. S. Tucson: The University of Arizona Press. pp. 703–737.
- Wasson J. T. and Kallemeyn G. W. 1988. Composition of chondrites. *Philosophical Transactions of the Royal Society of London A* 325:535–544.
- Yin Q. Z., Jacobsen S. B., Lee C. T., McDonough W. F., Rudnick R. L., and Horn I. 2001. A gravimetric K_2OsCl_6 standard: Application to precise and accurate Os spike calibration. *Geochimica et Cosmochimica Acta* 65:2113–2127.
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