Chondrules as direct thermochemical sensors of solar protoplanetary disk gas

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Chondrules, millimeter-sized igneous spherules comprising the major component of most chondritic meteorites, formed during the first 4 million to 5 million years of the evolution of the solar protoplanetary disk and, therefore, can potentially offer important constraints on the conditions in the disk, provided that the processes that led to their formation can be understood. High-resolution cathodoluminescence (CL) survey of chondrules from various chondrite groups revealed changes of CL activator concentrations of magnesium-rich olivines. We show that these overlooked internal zoning structures provide evidence for high-temperature gas-assisted near-equilibrium epitaxial growth of olivines during chondrule formation. We argue that this interaction with the surrounding gas, rather than various cooling histories, defined chondrule composition and texture. Chondrules are thus direct thermochemical sensors of their high-temperature gaseous environment, and high partial pressures of gaseous Mg and SiO are required in their solar protoplanetary disk-forming region to maintain olivine saturation in chondrules. The inferred crystallization of olivines, from stable melts approaching equilibrium with the surrounding gas, provides an explanation for the notable absence of large and systematic isotopic fractionations in chondrules.

**INTRODUCTION**

Chondrules are one of the major constituents (1–4) of chondritic meteorites (chondrites), which represent fragments of parent bodies populating the main asteroid belt. Chondrules are believed to have formed by melting of solid precursors in dust-rich regions of the protoplanetary disk during transient heating events of still unknown nature; both nebular and planetary mechanisms are being debated. Although shock waves in the protoplanetary disk (5, 6) are currently the most favored heating mechanism, chondrule formation by protoplanetary impacts is recently gaining interest (7).

One of the most fundamental aspects of chondrule formation is that chondrules (or rather, their precursors) were heated to high temperatures capable of producing significant melting and then cooled quickly enough to preserve a range of disequilibrium features. Any viable mechanism of chondrule formation must be able to reproduce thermal histories of chondrules (5), which can be deduced by studying the petrology and the mineral chemistry of natural chondrules and their experimental analogs. Dynamic crystallization experiments have successfully reproduced chondrule textures and therefore, until recently, provided the main constraints on peak temperatures and cooling rates of chondrule melts (8).

Here, we challenge this view by demonstrating that chondrule melts communicated with the surrounding gas, that is, behaved as an open system, and that formation of chondrule olivine grains was controlled by gas-assisted epitaxial growth. Although it is generally accepted that chondrules interacted with their surrounding gas, this paper goes further in suggesting that this interaction defines their composition and texture.

**RESULTS**

**CL zoning of magnesian olivines in chondrules**

Theory of cathodoluminescence (CL) (emission of photons following injection of high-voltage electrons that promotes valence electrons to conduction band) predicts that intrinsic CL of minerals is enhanced by defects and structural imperfections in the lattice and/or by substitutional or interstitial elements, which distort the lattice, that is, “CL activators.” Few elements, called “CL quenchers,” with Fe\(^{2+}\) being the most common, can play the opposite role in modifying the energy-level arrangement so that the CL process does not operate or is diminished. As long as CL quenchers are low in concentration, high-resolution CL may allow us to resolve very subtle changes of concentrations of CL activators, for example, few parts per million.

Here, we report on high-resolution CL survey of magnesium-rich porphyritic and barred olivine chondrules from several weakly metamorphosed ordinary and carbonaceous chondrites [Semarkona (LL3.0), GRA95229 (CR2), Y-81020 (CO3.0), DOM 08004 (CO3.1), Acfer 094 (C3.0 ungrouped), Allende (CV3.6), and Vigarano (CV3.1-3.3)] using high-resolution CL facility mounted on a field emission gun scanning electron microscope (FEG-SEM) (JSM-7000F, JEOL) equipped with a MonoCL A GATAN monochromator.

Comparison of backscattered electron (BSE) images obtained by FEG-SEM against high-resolution CL images of the same chondrules (Figs. 1 and 2; see section S1 for mineral and texture descriptions and abbreviations) shows the quantum difference between these two electron-matter interaction observation types. High-resolution CL images of these chondrules reveal internal structures of Mg-rich [Mg/(Mg + Fe) > 0.98]) olivines and low-Ca pyroxenes at a hitherto unprecedented detail.

In porphyritic and barred chondrules representing more than 90% of all chondrules in both ordinary and carbonaceous chondrites, high-resolution CL images reveal complex internal zoning patterns in nearly all Mg-rich olivines surveyed (Figs. 1 and 2 and section S1). These characteristics contrast with the unzoned low-Ca pyroxene CL features (Figs. 1A and 2B) that present exceptionally well-resolved striated microstructures of thin alternations of orthoenstatite and clinoenstatite in response to the ortho-clino inversion upon cooling (9). Glassy mesostasis and glassy inclusions in olivines show variable CL intensity (different gray tones), while metal has no CL emission and appears black in the CL images.

Each single Mg-rich olivine is composed of a core region surrounded by successive concentric layers of olivine that terminate by a euhedral faceted shape when olivine is bathed in the glassy mesostasis (Figs. 3A...
The inner core shows different zones with variable CL intensities. In porphyritic chondrules, the cores of the vast majority of olivines are characterized by a relatively low but variable CL intensity showing convoluted zones with embayment. These cores are sprinkled with various proportions of metal blebs and, in some cases, of Ca-Al-rich silicate glass inclusions hosting metal blebs themselves (Figs. 1 and 4 and table S1). In large Mg-rich olivine phenocrysts from larger chondrules (Fig. 2 and section S1), the core is made up of a patch of unzoned olivines with high CL intensity, which frequently host one or few euhedral spinel (MgAl$_2$O$_4$) inclusions (table S1). In all cases, however, an outer core surrounds and truncates the inner embayed regions. It is composed of one or several concentric olivine layers of variable thickness, showing alternations and oscillations of different CL intensities; truncations between layers are frequent (Figs. 2 and 4). The edge zone of an olivine grain is often euhedral with the lowest CL intensity (the darkest) in response to a significant decrease in CL activator/CL quencher ratio due to Fe enrichment. This edge zone systematically truncates with clear angular unconformity the faint structures forming the inner/outer core region (Fig. 4 and section S1). In an igneous object-like chondrule, each truncation/unconformity marks a “fossilized” dissolution surface separating two successive episodes of Mg-rich olivine growth. Growth episodes operate according to an epitaxial mode, as indicated by the well-preserved constant crystallographic orientations throughout the different shells/layers constituting the same olivine (Fig. 2C). It is also remarkable that two contiguous olivine layers have very low lattice mismatch, as determined by electron backscattered diffraction (EBSD) measurements (section S3).

Another striking feature revealed by the CL images is a well-defined asymmetric grain growth of olivines at chondrule margins (Figs. 1 to 3). These grains, showing similar core-to-edge zonation to other grains in the center of the chondrules, present a large asymmetric grain growth toward the free surface of the chondrule (Fig. 3). This asymmetric grain growth (that is, grain size increase) is associated with grain boundary migration driven by surface energy reduction. This often leads to olivine...

Fig. 1. High-resolution CL images of representative type I chondrules. See sketch in section S1 of the important features to be observed. (A and C) Yamato 81020, CO3.05, Ch#30b. This porphyritic olivine (ol) pyroxene chondrule shows the complex CL figures in each olivine with a core and euhedral outer edges. Olivine cores always contain metal (met) and glassy (gl) inclusions. This porphyritic olivine pyroxene chondrule shows an example of the Mg-rich olivine core with asymmetric overgrowth toward the periphery of the chondrule, forming a more or less continuous shell of the Mg-rich olivine at the outer edge, formed by successive olivine overgrowth layers. Low-Ca pyroxene (px) postdates the olivine growth. (B and D) Yamato 81020, CO3.05, Ch#9. Barred olivine chondrule. CL images allow us to resolve the first dendritic growth of each olivine bar in this chondrule. Notice the notable absence of FeNi metal blebs in olivine bars. The olivine rim that partly covers the chondrule surface corresponds to a multilayer Mg-rich olivine shell, similar to those observed at the outer edge of porphyritic chondrule. The unconformity between the shell and the olivine bars and their common crystallographic orientation suggest that the Mg-rich olivine shell formed after the olivine bars by an epitaxial growth mechanism.
aggregates with subparallel growth, columnar-like textures (Fig. 3A), triple junctions, and granoblastic textures (Fig. 3, B and C, and section S1), generated by the two- and three-dimensional (2D and 3D) competition for space, respectively. Some of these olivines acquire an extrava-
sated shape, which eventually may cover part of the 3D outer surface of
the chondrule (Fig. 1A and section S1). Resulting from the superposi-
tion of micrometer-sized Mg-rich olivine layers parallel to the chon-
drule surface (Figs. 2 and 3), such an asymmetrical growth contrasts
with known magmatic-like crystallization. From one crystal to another,
by grain boundary between two neighboring olivines, delineate a more
or less continuous olivine shell surrounding the whole chondrule (Figs.
1A and 3, B and C, and section S1). The low concentration of defects is
another remarkable characteristic of these olivines. When present, low-
Ca pyroxene in the outermost shell of the chondrules corrodes the
underlying olivine (with their complex CL structures), as outlined by
their poikilitic textures (Figs. 1 and 2). This suggests the late crystalliza-
tion of low-Ca pyroxene with respect to the Mg-rich olivine.

Corresponding to 10 to 15% of all the chondrules in both CC and
OC chondrites, barred olivine chondrules are formed by olivine bar

Fig. 2. High-resolution CL images of representative type I chondrules. (A) Vigarano, CV3, Ch#25. Barred olivine chondrule with high CL dendritic growth in olivine bars and
the thick and complex multilayer Mg-rich olivine shell at chondrule edge. (B) Yamato 81020, CO3.05, Ch#8. Porphyritic olivine pyroxene chondrule showing heterogeneous grain
size with a large porphyritic grain. CL zoning textures in the small olivine grains are similar to those preserved at the edge of the large porphyritic grain. Low-Ca pyroxenes are
characterized by CL well-resolved striated microstructures of ortho-clino inversion. Inset: Elemental map Al Ks x-ray showing the remarkable correspondence between Al concen-
tration and CL intensity map. Notice, however, the small rotating shift between the two images. (C) Vigarano, CVRed 3.3, Ch#4. Details of a euhedral Mg-rich olivine bathed in the
glassy mesostasis of a porphyritic olivine chondrule. Notice the several crystallization and dissolution fronts despite the euhedral shape of the whole crystal. These CL images also
reveal that olivine overgrowth episodes proceed by epitaxial growth on preexisting remnant grains. (D) DOM 08004, CO3.1, Ch#8. Mg-rich olivine grain showing multiple fronts of
dissolution and growth. Notice that the high CL intensity recorded by the olivine core is similar to Ch#8 in (B). (E) Yamato 81020, CO3.05, Ch#25b. Porphyritic olivine pyroxene
chondrule. Notice the significant difference between CL features of the Mg-rich olivines and the low-Ca pyroxenes, and that low-Ca pyroxene growth postdates the Mg-rich
olivine. Mg-rich olivine grains show several dissolution fronts. Unzoned low-Ca pyroxene CL features present exceptionally well-resolved striated microstructures of thin alter-
nations of orthoenstatite and clinoenstatite in response to the ortho-clino inversion upon cooling.

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crystals that are platy in three dimensions and have an olivine rim that partly covers the chondrule surface. These olivine rims have crystallographic orientation similar to the inner olivine platelets. High-resolution panchromatic CL survey reveals that each olivine bar is systematically devoid of metal bleb inclusions (Figs. 1 to 4 and section S1). Each bar instead hosts a brighter CL-elongated core that delineates a more or less continuous olivine shell surrounding the whole chondrule. Dissolution and overgrowth fronts similar to those observed in porphyritic chondrules (Figs. 1 and 2). Similarly, edges of olivine bars are euhedral with faceted shapes in contact with the glassy mesostasis and characterized by a low CL intensity due to Fe enrichment (section S1). At the chondrule border, the olivine rim of variable thickness is constituted by an almost continuous and circular rim of concentric micrometer-sized layers of Mg-rich olivines, similar to those surrounding porphyritic chondrules. While preserving the same crystallographic orientation, it is remarkable that the olivine bars and the olivine rim present frequently an angular unconformity relationship, suggesting that part of the olivine rim formed after the olivine bars using the bars as...
Similarly to porphyritic chondrules, low-Ca pyroxene, when present, forms the outermost shell of the barred olivine chondrules with poikilitically enclosed olivines.

While metal is featureless in CL, its contrast with respect to the CL intensity of olivine outlines other major unseen features in chondrules. If micrometer-sized metal blebs are omnipresent in the inner core of olivine grains from porphyritic chondrules, then they are clearly absent in olivine bars of barred chondrules (Figs. 1B, 2A, and 3D). In several chondrules (Fig. 4), FeNi metal droplets are pinched by the growth of the Mg-rich olivine, indicating explicitly that FeNi metal blebs were liquid at the time of Mg-rich olivine crystallization. The absence of CL quenching at the olivine-metal interface is remarkable. (C) Yamato 81020, CO3.05, Ch#9. Euhedral Mg-rich olivine with a core (low CL) sprinkled by both FeNi metal inclusions and Ca-Al-rich melt inclusions in a porphyritic olivine pyroxene chondrule. Some glass inclusions host spherical metal beads. (D) Acfer 094, CO3.1, Ch33b. Porphyritic olivine chondrule with large euhedral grain of Mg-rich olivine hosts a glass inclusion, which, in turn, hosts spherical FeNi metal blebs, suggesting the minimization of surface energy of two immiscible liquids.

Comparisons of the panchromatic CL images with high-resolution x-ray elemental area maps together with hyperspectral scans and individual spectra (Fig. 2B and section S2) (13–15) reveal that panchromatic CL intensity in Mg-rich olivines is overwhelmingly controlled by their Al concentration: The higher the panchromatic CL intensity, the higher their Al concentration (section S2). In terrestrial olivines, Al occurs at minor to trace levels (tens to hundreds of parts per million), and Al in Mg-rich olivines in chondrules is highly variable with concentrations up to 0.6 weight % (wt %) Al₂O₃ (table S1) (10, 16). Witnessing highly refractory melts, these high Al concentrations in chondrule olivines are consistent with (i) olivine-melt partitioning data (16, 17) and compositions of glassy inclusions in olivines or chondrule mesostasis that may contain up to 30 wt % Al₂O₃ (table S1), and (ii) the common presence of spinel (MgAl₂O₄) inclusions in magnesium olivines of type I chondrules indicative of melt compositions close to spinel saturation (section S2 and table S1) (18). Diffusion of tetrahedral Al is as slow as
that of Si; on average, diffusing two to four orders of magnitude slower than most other elements (19), the observed CL pan-
chromatic internal structures in Mg-rich olivines and their related
Al faint concentration variations used as a poorly diffusive (motion-
less) marker (Figs. 1 to 4) tell a complex story of the chondrule melt
from which they crystallized.

DISCUSSION
Evidence for gas-assisted epitaxial Mg-rich olivine growth
process during chondrule formation
There are several hints that olivine crystallization in chondrules results
from an overlooked nonconventional igneous process. These include
the following: (i) the high enrichment of an incompatible element like
Al in Mg-rich chondrule olivines (DAlo3 olivine-melt < 10−3; a similar trend
has also been observed for rare earth elements (20) in a much higher
proportion than anything else seen in terrestrial magmas, (ii) the
evidence for repeated olivine dissolution-crystallization episodes, (iii) the
asymmetric growth of Mg-rich olivines with columnar-like textures at
porphyritic chondrule edge, and (iv) the occurrence of Mg-rich olivine
shell composed of several micrometer-sized concentric layers
surrounding both porphyritic and barred chondrules. Low-Ca pyrox-
ene at chondrule edges has been interpreted as the result of gas-melt
interaction (21, 22), during which their crystallization results from the
partial dissolution of olivine due to the elevated silica activity in the melt
in response to the high partial pressure of SiO(g) of the surrounding gas.
Here, this asymmetric grain growth and/or deposition of Mg-rich oli-
vine concentric shells/layers toward the free surface of chondrules im-
ply, in a similar manner, that the surrounding gaseous environment is
very likely the main source of Mg, Si, and O atoms constituting the ma-
jor part of the Mg-rich olivines and hence of chondrules.

In the following section, we show how a gas-assisted epitaxial growth
mechanism (section S4), a variant of the vapor-liquid-solid mechanism
of single crystal growth (20, 23–25), can be applied as a phenomeno-
logical model to Mg-rich olivine growth in both porphyritic and
barred chondrules (Figs. 5, A and B, and 6). Predating the crystalliza-
tion of any Mg-rich olivine core in porphyroclastic chondrules, refractory-
rich silicate liquid droplets with different amounts of liquid FeNi metal
blebs scattered therein, for example, now seated as Ca–Al–rich silicate
glass and Fe–Ni metal inclusions in CL-characterized Mg-rich olivine
cores (Fig. 4 and table S1), are the most pristine condensed matters in
chondrules to which we can access using only textural characteristics (Fig.
5A). From McSween (26), we know that Ca–Al–rich glass inclusions
with their anorthite normative signature are clearly out of equilibrium
with their host Mg-rich olivines and that olivine is not its liquidus
phase (table S1) (21). Hence, it follows that interaction with the vapor
phase, by favoring preferential dissolution of Mg(g) and SiO(g) into the
liquid phase, is unavoidably the most efficient process to turn refrac-
tory melt compositions into olivine saturated ones to promote the
effective crystallization of the Mg-rich olivine according to the reaction
of the type

\[
\text{Ca–Al-rich melt} + \text{Mg}_8(g) + \text{SiO}_8(g) + \text{O}_2(g) = \text{Mg}_2\text{SiO}_4-\text{saturated melt} \tag{1}
\]

Chondrule melt also hosts various amounts of sodium (27); therefore, it
must be noticed that the enhancement of Mg-rich olivine saturation
from Ca–Al–rich refractory melts is very likely helped by an effect of so-
dium, which, by reducing the abundance of Si–O–Si linkages in the melt,
that is, decreasing the silica activity of the melt, αSiO₂, favors the stabil-
ization of depolymerized phases like olivines (28). If 12 to 15 wt % MgO
are needed in CaO–MgO–Al₂O₃–SiO₂ melts to reach Mg-rich olivine sat-
uration (21), then only less than 5 to 6 wt % MgO are necessary for sta-
bilizing Mg-rich olivines in a CaO–MgO–Al₂O₃–SiO₂–Na₂O melt at high
temperature. According to Le Chatelier’s principle, any disturbance in gas
partial pressures [for example, PMgO, PSiO₂, PO₂, and, possibly, PNa(g)
in the immediate vicinity of the chondrule will promote the back-and-
forth reaction (Eq. 1), either in the condensation/solubility/olivine crystalli-
zation direction toward the right-hand side or in the evaporation/olivine
dissolution direction toward the left-hand side (Fig. 5).

Nucleation and growth theory states, however, that spontaneous
 crystalization from a melt will not start at saturation but only when
the solution becomes supersaturated (section S5). Homogeneous nu-
cleation has a large energy barrier, which is easier to overcome at a higher
level of supersaturation. This is why significant degrees of undercooling
(8, 29, 30) are generally invoked for olivine crystallization
in chondrule melts (Fig. 6). By increasing the degree of undercooling
(for example, cooling rate), it was shown experimentally that the
olivine habit evolves following the sequence: polyhedral, skeletal, and
dendritic (29–32), matching well with porphyritic and barred
textures depicted in chondrules.

Our CL survey allows us to challenge this classical view by noticing
that none of the Mg-rich olivine crystals in porphyroclastic chondrules pre-
serves evidence of dendritic growth, followed by ripening toward a poly-
hedral habit, as it should be in the case of undercooled supersaturated
melts (section S5) (32). In contrast, olivine bars in barred chondrules do.
The unique occurrence of FeNi metal blebs in the core region of Mg-
rich olivine crystals of porphyroclastic chondrules, together with concentric
Mg-rich olivine overgrowths around them (Fig. 4), instead suggests that
seeding is critical in the crystallization behavior of porphyroclastic
chondrules (S5), but not in their barred equivalents (Fig. 3B).

We thus suggest that the main difference in textures of type I chon-
drules, that is, porphyritic or barred (Fig. 5), is linked to the presence or
absence of FeNi metal blebs acting as a seeding agent during the crys-
tallization of Mg-rich olivines, in which conditions close to Mg-rich ol-
vine saturation were maintained in the chondrule melt by adequate gas
partial pressures from the surrounding environment (Eq. 1). In re-
sponse to FeNi metal seeding (very likely as liquid droplets), only very
small undercooling (as small as only a few kelvins) below the saturation
temperature (or melt supersaturation at saturation temperature by the
gas phase; section S5) will be needed to promote a polyhedral crystal
growth of olivine. The overgrowth crystal faces are in near equilibrium
with the host liquid, and future porphyritic textures are anticipated. In
the absence of FeNi metal seeding, as is the case in barred chondrules,
the same conditions of undercooling below the saturation temperature
(or supersaturation of the melt by the vapor phase at saturation tem-
perature; see section S5) instead promote skeletal, hopper shape, and
dendritic crystal growth of the Mg-rich olivine at the near edge of the
chondrule, very likely in response to the centripetal Mg and Si gradients
(33). After dendritic growth, the dendritic olivine crystal ripened slowly
toward a polyhedral habit in conditions approaching equilibrium in a
manner similar to polyhedral crystal (Figs. 1B, 2A, and 3D and section
S5) [figure 17 in (32)]. A necessary condition for epiaxial growth is the
absence of strong cooling and heating cycles, because large temperature
fluctuations are known to yield typical crystal habits (closed hopper and
complex swallowtail) that are not observed in barred olivine overgrowths.

In the course of further crystallization in both barred and porphyritic
chondrules, Mg-rich olivine cores and their overgrowth reveal, as we have

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shown (Fig. 4), complex CL microstructures indicative of faint and irregular Al concentration variations delineating several crystallization and dissolution fronts in each individual Mg-rich olivine. Despite their complexity, these microstructures can be well understood in the framework of this gas-assisted epitaxial growth mechanism (Fig. 5 and Eq. 1). Three main steps can be distinguished: (i) the incorporation step, comprising the adsorption and cracking of the vapor species—$PMg_{(g)}$, $PSiO_{(g)}$, $PNa_{(g)}$, and $PO_{2(g)}$—by disproportionation reactions at the surface of the liquid droplet, leading to a supply of the corresponding species to the (Ca-Al–rich) liquid; (ii) the diffusion step, describing the diffusion of the vapor species into the liquid; and (iii) the crystallization step, where the vapor species are incorporated into the olivine crystal lattice. We suggest that the main difference in the textures of type I chondrules, that is, porphyritic or barred, is linked to the presence or absence of FeNi metal blebs. In porphyritic chondrules, the FeNi metal blebs act as a seeding agent during growth mechanism of the Mg-rich olivine. In the case of barred chondrules, Mg-rich olivine growth starts at the edge of the chondrule (thin layer) and is followed by a dendritic growth in a given crystallographic direction toward the inside of the chondrule in response to the inward Mg and Si chemical gradient (34). The dendritic step of growth is very similar to the one depicted in Al-rich chondrules (figures 1 and 2 in (10)). The current growth mechanism can be divided in three main steps: incorporation, diffusion, and crystallization (see text). In this cartoon, the pristine Ca-Al–rich melt (dark blue) is progressively diluted by MgO and SiO$_2$ components entering the chondrule melt from the gas phase (pale blue and then yellow) (see Eq. 1).

**Fig. 5. Gas-assisted near-equilibrium (liquid epitaxial) growth of Mg-rich olivines.** (A), porphyritic olivine chondrules; (B), barred olivine chondrules. We suggest that the main difference in the textures of type I chondrules, that is, porphyritic or barred, is linked to the presence or absence of FeNi metal blebs. In porphyritic chondrules, the FeNi metal blebs act as a seeding agent during growth mechanism of the Mg-rich olivine. In the case of barred chondrules, Mg-rich olivine growth starts at the edge of the chondrule (thin layer) and is followed by a dendritic growth in a given crystallographic direction toward the inside of the chondrule in response to the inward Mg and Si chemical gradient (34). The dendritic step of growth is very similar to the one depicted in Al-rich chondrules (figures 1 and 2 in (10)). The current growth mechanism can be divided in three main steps: incorporation, diffusion, and crystallization (see text). In this cartoon, the pristine Ca-Al–rich melt (dark blue) is progressively diluted by MgO and SiO$_2$ components entering the chondrule melt from the gas phase (pale blue and then yellow) (see Eq. 1).
of the species (Si, O, Mg, Na) through the droplet and their putative mixing with the initial Ca-Al–rich silicate melt; and (iii) the crystallization step, characterizing the growth of Mg-rich olivine crystals either on the FeNi metal seeds in porphyritic chondrules or at the liquid-vapor interface in barred chondrules.

During a steady-state episode of growth \((dG < 0)\), the chemical potential, that is, \(\mu_i = (dG/dn)_T. P. n_i\) of the vapor (v or g), liquid (l), and solid (s; for example, Mg-rich olivine) phases must obey the following chemical potential cascade, for which \(\mu_v > \mu_l > \mu_s\), respectively (Fig. 5). It is thus very likely that the various crystallization and dissolution fronts, as delineated by CL intensity oscillations and microstructures in the Mg-rich olivines (Figs. 1 and 2), bear witness of subtle variations in vapor partial pressures, temperature, and/or chemical composition of the liquid occurring in the ambient vapor and in the crystallizing chondrule according to the back-and-forth reaction (Eq. 1) and its control on olivine/melt trace element partitioning, including \(D_{Al}\). These temperature, pressure, and melt elemental concentration variations are expected to be small due to the near-equilibrium conditions preserved during the whole range of Mg-rich olivine crystallization.

Finally, it is worth noticing that epitaxial growth mode is known to reduce the surface energy, leading to complete wetting of the surface and thus the deposition of successive low defect layers of Mg-rich olivines, with low crystallographic mismatch, as observed in both porphyritic and barred chondrules (section S3). The epitaxial growth mode, that is, 2D morphology Frank–van der Merwe layer-by-layer growth mode (section S6) (34), is thus very likely the process responsible for multi-layer Mg-rich olivine shells at the edge of both porphyritic and barred chondrules. If a system having a continuous change from vapor and/or liquid to solid cannot be at equilibrium, then the recognition of such an epitaxial growth mode hints yet in favor of near-equilibrium conditions.

**Fig. 6. Chondrule thermal history.** (A) Summary of chondrule heating and cooling conditions from experimental constraints (8). Cartoon showing maximum temperature relative to the liquidus, for (from right to left) porphyritic, barred, and radial textures, as expected from dynamic experiments. In general, porphyritic textures are produced when the peak temperature is below the liquidus, thus preserving multiple nucleation sites. Barred textures are produced when the peak temperature is slightly above the liquidus temperature such that most, but not all, nucleation embryos are destroyed. Radial textures are produced from temperatures that exceed the liquidus temperature, and in which few or no nucleation sites are available. (B) Current two-stage nonlinear cooling rate thermal history model for chondrule formation. The temperature difference between porphyritic and barred chondrules is related to the presence or absence of FeNi metal droplets acting as seeds; the melt is maintained near Mg-rich olivine saturation due to high partial pressures: \(P_{Mg(g)}, P_{SiO(g)}\), and very likely \(P_{Na(g)}\) of the surrounding gaseous environment. In contrast with the previous model (A), chondrules cool fast after a variable, but short (few tens of minutes maximum), time of near-equilibrium crystallization governed by gas-melt interaction at elevated temperatures of \(\geq 1800\) K. This model establishes the preponderance of the high-temperature gas-melt interaction to define the composition and texture of chondrules and that chondrules did not stay hot very long. Blue, melt; green, Mg-rich olivine; gray, low-Ca pyroxene.
Chondrule formation and thermal history

The presented microstructures in Mg-rich olivines open the door to new perspectives for solving the vexing enigma posed by chondrules for at least 14 decades (35). They provide evidences for high-temperature gas-assisted near-equilibrium crystallization and epitaxial growth of olivines during chondrule formation. That FeNi metal was liquid at the time of Mg-rich olivine crystallization (Fig. 4) states unequivocally that their crystallization temperatures in type I chondrules are in the range of 1800 K or above, that is, \( T_{\text{melting}} > 1773 \) K for Fe\(_{0.8}\)Ni\(_{0.2}\) and 1830 K for pure Fe; such high temperatures favored, in turn, diffusion and mass transfer processes in the chondrule-gas system (Fig. 5).

In the present model, the texture difference between porphyritic and barred chondrules is simply related to the presence or absence of FeNi metal droplets acting as seeds; the melt is maintained near Mg-rich olivine saturation due to high partial pressures: \( \text{PMg}(g) \), \( \text{PSiO}_2(g) \), and very likely \( \text{PNa}(g) \) of the surrounding gaseous environment (section S7), as suggested by the ubiquitous successions of episodes of Mg-rich olivine dissolution and epitaxial (over)growth. The bulk composition of chondrules, in turn, is controlled by the duration of gas-melt interaction and the partial pressures reigning in the gaseous environment (Eq. 1; see below).

Low-Ca pyroxenes in chondrules (8, 21, 22) explicitly postdate Mg-rich olivine crystallization, as indicated by the poikilitic enclosure of the Mg-rich olivine with their CL zoning features (Figs. 1 and 2). The CL well-resolved thin alternations of orthoenstatite and clinoenstatite in most of the low-Ca pyroxenes suggest rapid cooling conditions, as indicated by the ortho-clino inversion upon cooling (9), with higher cooling rates (\( > 10^3 \) K/hour below \( \approx 1273 \) K) documented at elevated clino/ortho modal ratios. Together, the CL features of olivine and low-Ca pyroxene allow us to propose a two-stage nonlinear cooling rate thermal history for both porphyritic and barred chondrules (Fig. 6): low cooling rates of only few kelvins per hour at olivine saturation and a progressive increase toward fast cooling rates during low-Ca pyroxene crystallization (36). Likewise, the asymmetric grain growth and the multilayer shell of olivines at chondrule margins (Fig. 3) are indicative of a higher rate of olivine crystallization and could have been promoted by the slight increase in the supersaturation of the system due to faster cooling. Fast terminal cooling rates are also required to preserve the figures of FeNi metal droplets pinched by the growth of the Mg-rich olivine (Fig. 4), the occurrence of relict grains, and/or sharp chemical zoning in olivines, the latter being estimated in the range of \( 10^2 \) to \( 10^6 \) K/hour (37, 38). Similar conditions of fast cooling are needed to quench the silicaceous poor melt liquids bathing chondrule crystals into glasses (Figs. 1 to 4).

At odds with models inferred from dynamical experiments (Fig. 6), Mg-rich olivines in chondrules result from near-equilibrium crystallization due to saturation of the chondrule melt by the gas phase at elevated temperatures of \( \geq 1800 \) K (Eq. 1) and not from the various cooling rates as is generally inferred [that is, cooling rates vary by almost three orders of magnitude from 1 to 10 K/hour to (2 to 3) \( \times 10^5 \) K/hour] to reproduce the main chondrule textures (Fig. 6) (5, 8). That is, we infer that porphyritic and barred olivine chondrules with their seeded/nonseeded differences have been shaped mainly by high-temperature gas-melt interactions and that they both record similar thermal histories. In both cases, low-Ca pyroxene crystallization records the end of these interactions and the start of the more or less rapid cooling or the quench of chondrule melt (Fig. 6). The time spent at high temperature for crystallization of Mg-rich olivines must be short. From Fe-Mg interdiffusion data (39), the very limited diffusion of iron at metal-olivine boundaries in olivine grains, as depicted by the absence of CL quenching features (Fig. 4), precludes the possibility that chondrules spent time in excess of a few tens of minutes at temperatures in the range of 1800 K. Similarly, rapid dissolution rates for relict olivine grains also indicate a limited duration at high temperatures for chondrules (40).

In contrast with the general idea that chondrules experienced slow-to-moderate cooling rates, for which they took hours or days to crystallize and solidify (5, 8), we advocate that chondrules cool fast after a variable, but short (few tens of minutes maximum), time of near-equilibrium crystallization governed by gas-melt interaction at elevated temperature (Fig. 6). Thus, chondrules did not stay hot very long.

Gas-melt interaction

Starting from Ca-Al–rich silicate and FeNi metal liquids whose origin remains to be specified, this model ascertains the preponderance of the high-temperature gas-melt interaction in controlling the composition and texture of chondrules. Accordingly, chondrule composition (for example, Mg/Si\(_{\text{bulk}}\), Si/Al\(_{\text{bulk}}\), or Mg/Al\(_{\text{bulk}}\)), mineralogy (for example, olivine/pyroxene ratio), and texture (for example, barred versus porphyritic) are almost directly related to their high-temperature gaseous environments. A simple mass-balance calculation in a Mg/Si versus Al/Si compositional space between Ca-Al–rich liquids (glass inclusions) and bulk type I chondrule compositions (21) revealed that more than 60 to 70% of the chondrule composition originated from the gas phase, if \( \text{Al}/\text{Si} \approx 0 \) is assumed to represent the composition of the gas-assisted silicate phases, namely, Mg-rich olivine: Mg/Si = 2 (see Eq. 1) and low-Ca pyroxene: Mg/Si = 1. Mg-rich olivines crystallize first, and the SiO\(_2\)/PMg\(_{\text{bulk}}\) ratio must increase in the gas phase as crystallization proceeds, leading to lower olivine/pyroxene ratio and progressive decrease in Mg/Si\(_{\text{bulk}}\), chondrule composition.

From thermodynamic considerations (41), the inferred stability of both Ca-Al–rich, refractory liquid and Fe-Ni metal liquid ones before the crystallization of the Mg-rich olivine opens up the perspective that chondrules formed at high ambient gas pressures relative to canonical estimates for pressures in the inner solar nebula (\( P \approx 0.1 \) to 100 Pa). Pressures and/or dust concentrates in the chondrule-forming regions relative to a gas of solar composition (41, 42) remain difficult to assess and are well beyond the scope of this study. We notice, however, that regions with high pressure and low dust/gas ratio should be favored to form type I chondrules hosting almost pure forsteritic olivines, Fe-Ni metal liquid droplets bathed in Ca-Al–rich silicate liquids (table S1). If dust enrichment increases condensation temperatures at lower pressure, possibly to temperatures at which partial melts are stable, then it instead increases oxygen fugacity favoring fayalitic olivines at high temperatures.

The process reported here explains why, when they formed, chondrules were stable melts that approached high-temperature equilibrium with their high partial pressures [Mg\(_{(g)}\), SiO\(_2\)(g), and Na\(_2\)(g)] surrounding gas to maintain Mg-rich olivine saturation (section S7). This, in turn, provides a sound explanation for many of their textural and chemical characteristics, including the retention of volatile elements such as Fe, Mg, Si, Na, and K and the notable absence of large and systematic Rayleigh-type isotopic fractionations (43–45). These results open up the interesting perspective that any variability in chondrule chemical and isotopic compositions should not be considered as the result of the chondrule-forming process itself (for example, no marked evaporation) but instead reflects mixtures of different sources or heterogeneous starting materials.

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Reclit grains
Reclit grains, by definition, are grains that did not crystallize from a host chondrule melt. On the basis of the textures, mineralogy, and chemical and oxygen isotopic compositions, various kinds of coarse (>10 µm) reclit objects were identified in porphyritic chondrules; these include refractory inclusions and chondrules of earlier generations and their fragments and, possibly, fragments of thermally processed planetesimals (1). Depending on the host chondrule compositions, it is, however, more or less easy to ascertain the reclit nature of a grain or an agglomeration of grains (for example, similar Z number in BSE images) and, in any cases, to evaluate their real proportion.

In the proposed open-system scenario of chondrule formation, in which chondrule melt-gas interactions are the key process, the early crystallizing Mg-rich olivine phenocrysts could become out of equilibrium with the chemically and isotopically evolved chondrule melts and may appear reclit. Because FeO-poor type I chondrules are by far the most abundant chondrule type in chondrites, and because all Mg-rich olivines look the same with low Z-averaged number, we strongly advocate that high-resolution CL imaging should be considered as an indispensable prescreening tool for secondary ion mass spectrometry measurements (and other in situ analyses). The probability of finding reclit grains and measuring their real isotopic composition should be significantly increased. The detection of reclit olivine grains and the determination of their frequency in chondrites have important implications on the nature of putative chondrule precursors, their gaseous environment, and their mode of formation (46, 47).

Astrophysical setting for chondrule formation
Many melting mechanisms have been put forward over the last decades to explain the igneous textures of chondrules. This CL survey of porphyritic/barred chondrule brings new constraints for chondrule thermal history, which, in turn, have important implications for protoplanetary disk processes.

Requiring high partial pressures of Mg(g) and SiO(g) in the vapor phase to maintain Mg-rich olivine saturation, chondrules are inferred to be direct thermochemical sensors of their high-temperature gaseous protoplanetary environments of formation. At the smaller scale of a given chondrule or at larger scales from chondrules in a given chondrite, gaseous partial pressures and their variations during the chondrule formation process can thus be estimated. In addition, because diffusion time is very limited at temperatures in the range of 1800 K (Fig. 5), the almost ubiquitous alternations of dissolution and growth microstructures in Mg-rich olivines suggest that local regions of chondrule formation did not cool/evolved monotonically as very often assumed but rather have local oscillating variations superimposed on the overall falling temperature. Are these oscillations linked to convection in a falling temperature. Are these oscillations linked to convection in a whole using a charge-coupled device detector with a sensitivity range of 250 to 900 nm. Acquisition time was fixed to 10 s/pixel.

Among the competing models of chondrule formation (5–8), nebula shocks due to gravitational instability shock heating or bow shock from planetesimals (5, 6) are currently the most favored heating mechanisms (Fig. 6). In these shocks, it is generally assumed that primordial dusty materials were flash-heated from ambient temperatures (<600 K) to above liquidus temperature (1600 to 2000 K). Cooling rates from peak temperature are very high (>10^4 K/hour) and then slow down to ~10^1 to 10^2 K/hour in relation to the optical depth or the dust/gas ratio of the medium, with slower cooling rates (1 to 50 K/hour) at lower temperatures close to the glass transition temperature (T_g). For individual chondrules, heating duration from the peak temperature down to the closure of the system at T_g, must have varied between several hours to several days. Assuming that constraints on the thermal histories of chondrule are diagnostic (5), large-scale nebular and bow shocks predict thermal histories that are not consistent with our inferred two-stage nonlinear cooling rate thermal history and specifically with the fast cooling rates responsible for the quench of the chondrules. In contrast, impact splashes during planetesimal recycling (48) or electric discharges in dusty gas clumps (49) favoring chondrule formation by radiative cooling processes, for example, on the order of hundreds of kelvin in 1 min or 10^4 K/hour after the lightning bolt (49), match this new chondrule thermal history quite well and deserve to be explored in more detail.

Protoplanetary disks are optically thick at most wavelengths (50), and only the surface layers or the optically thin outer regions may provide observations of dust and gas. In contrast, chondrules from chondrites of our solar system may provide, if our interpretation is correct, our best proxy of the gas phase present in the optically thick inner and planet-forming regions of young stellar objects.

MATERIALS AND METHODS
A high-resolution CL setup was mounted on a FEG-SEM (JSM-7000F, JEOL) [MonoCL4 GATAN monochromator equipped with both a high-sensitivity array detector and a high-sensitivity photomultiplier, suitable both for hyperspectral analyses and for panchromatic and monochromatic imaging; Centre de Recherches sur l’Hétéro-Epitaxie et ses Applications (CRHEA), Valbonne, France]. Collection of integrated luminescence extracted from the sample was achieved using a paraboloidal mirror placed above the sample. Electron beam was directed perpendicularly to the sample surface through a hole in the center of the mirror. For panchromatic imaging, recording was achieved using a high-sensitivity photomultiplier detector. Electron beam current used in the study ranged typically from 1 to 4 nA, and voltage beam was fixed at 5 keV. For this accelerating voltage, the emitting volume expanded up to 230 nm below the bombarded sample surface and around 200 nm sideways, assuming a 100-nm graphite coating thickness on chondrite thin sections. To avoid as much as possible CL “hot spot” effect, which was particularly effective at low magnification, recording was made with sample placed lower than focal plane of the paraboloidal mirror for magnifications less than ×500. For hyperspectral analysis, the extracted luminescence was directed toward a 300-mm focal length monochromator equipped with a 150 grooves/mm grating blazed at 500 nm; the entrance slit was fixed to 300 µm, which gave a spectral resolution better than 3 nm. Dispersed light was collected as a whole using a charge-coupled device detector with a sensitivity range expanding from 250 to 900 nm. Acquisition time was fixed to 10 s/pixel.

Both porphyritic and barred olivine chondrules from several weakly metamorphosed ordinary and carbonaceous chondrites—Seckamona (LL3.0), GRA95229 (CR2), Y-81020 and DOM 08004 (CO3.0), Acfer 094 (C3.0 ungrouped), Allende (CV3.6), and Vigarano (CV3.1-3.3)—were studied.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/7/eaar3321/DC1
Section S1. Further high-resolution CL images of chondrules
Section S2. Preliminary CL spectral analyses
Section S3. CL and EBSD in chondrules

Fig. S10. Principal modes of epitaxial growth resulting mainly from competition between
Fig. S8. Intracrystalline misorientations for Mg-rich olivine grains, as determined by EBSD.
Fig. S5. CL activator distribution in Mg-rich olivines in porphyritic olivine chondrules.
Fig. S4. CL spectral analysis of chondrule Mg-rich olivines.
Fig. S2. CL images of porphyritic chondrules from various chondrites.
Fig. S1. CL image abbreviations used in the text and figures.

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Figs. S1–S5.

Fig. S1. CL image abbreviations used in the text and figures.
Fig. S2. CL images of porphyritic chondrules from various chondrites.
Fig. S3. CL and EBSD in chondrules.
Fig. S4. CL spectral analysis of chondrule Mg-rich olivines.
Fig. S5. CL activator distribution in Mg-rich olivines in porphyritic olivine chondrules.
Fig. S6. Crystallographic fabrics of Mg-rich olivines in porphyritic olivine chondrule ch4 of Vigarano CV3.
Fig. S7. Crystallographic fabrics of Mg-rich olivines in porphyritic olivine chondrule ch4 of Vigarano CV3.
Fig. S8. Intracrystalline misorientations for Mg-rich olivine grains, as determined by EBSD.
Fig. S9. Epitaxial growth crystallization in a simplified binary diagram.
Fig. S10. Principal modes of epitaxial growth resulting mainly from competition between surface/interface energies.
Fig. S11. Tables showing the inferred chondrule formation steps.

Table S1. Examples of chemical composition of representative Mg-rich olivines and their associated phases from chondrule of Yamato 81020.

References (S1–S5)
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