Quasicrystals at extreme conditions: The role of pressure in stabilizing icosahedral $Al_{63}Cu_{24}Fe_{13}$ at high temperature

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Abstract

Icosahedrite, the first natural quasicrystal with composition $Al_{63}Cu_{24}Fe_{13}$, was discovered in several grains of the Khatyrka meteorite, a unique CV3 carbonaceous chondrite. The presence in the meteorite fragments of icosahedrite strictly associated with high-pressure phases like ahrensite and stishovite indicates a formation conditions at high pressures and temperatures, likely during an impact-induced shock occurred in contact with the reducing solar nebula gas. In contrast, previous experimental studies on the stability of synthetic icosahedral AlCuFe, which were limited to ambient pressure, indicated incongruent melting at ~1123 K, while high-pressure experiments carried out at room temperature showed structural stability up to about 35 GPa. These data are insufficient to experimentally constrain the formation and stability of icosahedrite under extreme conditions. Here we present the results of *in situ* high pressure experiments using diamond anvil cells of the compressional behavior of synthetic icosahedrite up to ~50 GPa at room temperature. Simultaneous high P-T experiments have been also carried out using both laser-heated diamond anvil cells combined with in situ synchrotron X-ray diffraction (at ~42 GPa) and multi-anvil apparatus (at 21 GPa) to investigate the structural evolution of icosahedral $Al_{63}Cu_{24}Fe_{13}$ and crystallization of possible coexisting phases. The results demonstrate that the quasiperiodic symmetry of icosahedrite is retained over the entire experimental pressure range explored. In addition, we show that pressure acts to stabilize the icosahedral symmetry at temperatures much higher than previously reported. Based on our experimental study, direct crystallization of Al-Cu-Fe quasicrystals from an unusual Al-Cu-rich melt would be possible but limited to a narrow temperature range beyond which crystalline phases would form, like those observed in the Khatyrka meteorite. An alternative mechanism would consist in late formation of the quasicrystal after crystallization and solid-solid reaction of Al-rich phases. In both cases, linking our results with observations in nature, quasicrystals are expected to preserve their

structure even after hypervelocity impacts that involve simultaneous high pressures and temperatures, thus proving their cosmic stability.

Keywords: Icosahedrite, Quasicrystals, CV3 chondrite, redox, Khatyrka meteorite, solar nebula.

Introduction

Quasicrystals (QC; Levine and Steinhardt 1984; Shechtman et al. 1984) represent a class of solids characterized by quasiperiodic translational order and forbidden rotational symmetries, such as the icosahedral (i) symmetry exhibited by $Al_xCu_yFe_z$ alloys, where x varies between 61 and 64, y is 24-26 and z 12-13 atomic% (Bancel 1999). This chemical interval corresponds to the compositional range at which the i-QC solely is stable up to ~1023 K at ambient pressure. Above this temperature the stability field of the quasicrystal decreases to a very narrow chemical composition up to ~1123 K, where the i-QC with composition $Al_{62.5}Cu_{25}Fe_{12.5}$ coexists with a liquid + (λ) monoclinic phase with composition $Al_{13}Fe_4$ (Tsai 2013; Zhan and Lück 2003a-e). At temperature above ~1200 K i-QC has been shown to be unstable, such that the liquid only coexists with the λ phase. At approximately 1300 K the system is totally molten and the liquid composition reflects that of the starting QC.

Experimental studies of the phase relationships at ambient pressure have been the only available tool available to date to constrain the origin of the first natural quasicrystal, icosahedrite $Al_{63}Cu_{24}Fe_{13}$ (Bindi et al. 2009). However, textural and petrographic evidence suggest that the natural quasicrystal formed in outer space under pressures and temperatures considerably higher than 1 bar and 1300 K (Bindi et al. 2012; Hollister et al. 2014). Recently, Stagno et al. (2014) performed *in situ* HP-HT X-ray diffraction studies and showed that the icosahedral symmetry of i-AlCuFe QC is retained at 5 GPa and temperature up to 1673 K. Above this temperature the

analogue of icosahedrite used for the experiments was found to decompose to a liquid in equilibrium with CuAl (corresponding to the mineral cupalite, an accessory phase also found in the Khatyrka meteorite), and the cubic β phase (Bindi et al. 2012). Although this study provided information on the compressional behavior of i-AlCuFe QC, the results gave only a lower-bound on the P-T stability of natural icosahedrite. Previous studies that focused on the compressional behavior and structural stability of QCs with compositions slightly different from that of icosahedrite include measurements on i-$Al_{62}Cu_{25.5}Fe_{12.5}$, which was shown to be stable up to 35 GPa (Sadoc et al. 1994, 1995; Lefebvre et al. 1995). The role of combined pressures and temperatures, however, remains to be explored.

Here we present experimental results using both diamond anvil cell (DAC) and multi-anvil techniques to investigate the stability of synthetic i-AlCuFe at higher pressure and temperature than those reported in previous studies. We show for the first time that the icosahedral structure is stabilized at high temperature as pressure increases, which makes quasicrystals behavior similar to that shown by crystalline materials when exposed to extreme conditions. Based on our results, icosahedrite might have formed within a large range of pressures and temperatures during the formation of our solar system under extremely reducing conditions, and Khatyrka might represent one of the many QC-bearing meteorites orbiting in our solar system or in other solar systems in the Milky Way and in galaxies throughout the cosmos.

EXPERIMENTAL METHODS

The synthetic icosahedral quasicrystal used as starting material was characterized by SEM and XRD measurements and shown to have the formula $Al_{63}Cu_{24}Fe_{13}$ (Bancel 1999) plus minor amounts of cupalite, (Cu, Fe)Al. The synthetic material was first broken in several small

fragments. A small cheap was, then, loaded in a diamond anvil cell with culet size of 600 μm and crushed to a fine powder by hand loading. A small portion of the powder with dimensions of about 30 × 30 μm was picked with a needle and placed at the center of a symmetric diamond anvil cell with 300 μm culet size using a Re gasket as sample chamber with a 150 μm diameter hole. A couple of ruby spheres were placed next to the sample as pressure markers. One diamond anvil was supported by a cubic boron nitride (c-BN) backing plate, and the other anvil by a tungsten carbide (WC) backing plate. *In situ* angle-dispersive powder X-ray diffraction measurements were performed at high pressure at the 16BM-D beamline, HPCAT (APS, Argonne). The DAC was loaded with neon as pressure medium also used as pressure marker (Hemley et al. 1989), and mounted on a motor driven stage with the WC seat on the downstream side, and the c-BN seat on the upstream side. Pressures inside the DAC was measured with the ruby luminescence method (Mao et al. 1986) with an on-line system. The used wavelengths of the monochromatic incident X-ray beam was 0.42460 Å and 0.5166 Å, respectively. The beam was focused to a focal spot of 5 x 15 μm by using a pair of Kirkpatrick-Baez mirrors. The MAR345 image plate detector was placed at a distance approximately of 478 mm from the sample in order to obtain high resolution and accuracy of the Debye-Scherrer diffraction rings. Diffraction peaks were collected using a continuous ω-oscillation scan mode over the range from -6° to +6° with an exposure time of 180 seconds.

Simultaneous high-pressure and temperature synchrotron powder X-ray diffraction experiments were conducted at the 13ID-D beamline of GSECARS (APS, Argonne) using a focused monochromatic X-ray beam of 30 KeV and with wavelength of 0.4133 Å. Double-side laser heating was performed using two focused infrared laser beams on both sides of the sample co-axially aligned with the incoming X-ray beam using the X-ray induced luminescence on the

112 sample. Laser power was adjusted independently on upstream and downstream sides to control
113 the measured temperature within ±100K. Heating durations at the target temperature was about
114 10 min. Temperatures of the laser-heated sample were measured using thermal radiation spectra
115 fitted to the blackbody radiation function (Prakapenka et al. 2008). Diffraction patterns were
116 collected on a MarCCD-165 Detector with exposure time of 15 s. In these experiments chips of
117 synthetic $Al_{63}Cu_{24}Fe_{13}$ were also crushed and then slightly pressed to form a platelet. A small
118 platelet with a diameter of approximately 60 μm was loaded into the sample chamber of a
119 symmetric diamond-anvil cell with flat anvils of 300 μm-size culet. Pressure was measured using
120 the thermal equation of state of Ne. The *in situ* X-ray diffraction patterns were processed using
121 FIT2D software (Hammersley 1998), and the *d*-spacing relative to each reflection was accurately
122 determined using PeakFit software.
123 Quench experiments were performed at 21 GPa and temperature between 1600 K and 2000 K
124 using a 1500-ton Walker-type press available at the Carnegie Institution of Washington. The
125 starting material used in this study is a synthetic icosahedral AlCuFe (≥99.9%) quasicrystalline
126 powder with nominal composition of $Al_{65}Cu_{23}Fe_{12}$ previously characterized (13). Tungsten
127 carbide anvils of 3 mm truncation edge length (TEL) were used with 8 mm edge length MgO
128 pressure media. Graphite and alumina capsules were used in the attempt to prevent oxidation of
129 the starting material. The capsules were then placed in the central portion of a cylindrical Re
130 furnace, surrounded by MgO sleeve and spacers. A $LaCrO_3$ sleeve was used as thermal insulator
131 outside the heater.
132 Details about the pressure calibration of the employed assemblies are reported in (Hirose and Fei
133 2002). The temperature during the experiment at 1973 K was monitored with a W-5%Re/W-
134 26%Re (C-type) thermocouple inserted within an alumina sleeve, with the junction in contact

with the top of the capsule. From this run a temperature versus power calibration curve was obtained and employed for the additional runs. The sample was compressed to the target pressure at a rate of 0.5 GPa/hr, then heated to the target temperature and kept manually constant within 10 K for a period of 15-60 minutes. The sample was quenched by turning off the power to the furnace and, then, decompressed to ambient pressure.

All recovered samples from quench experiments were mounted in epoxy resin and polished parallel to the axial furnace direction for textural observation and chemical composition mapping by Field Emission Scanning Electron Microscope (JEOL JSM 6500F). Semi-quantitative analyses using energy-dispersive X-ray spectroscopy, we performed at 15 kV and 1.1 nA employing metals (Fe, Cu, Al,) and oxides (Al_2O_3) as standards. Phase identification of the selected recovered run products was accomplished using an Oxford Diffraction Xcalibur PX Ultra single-crystal diffractometer fitted with a 165 mm diagonal Onyx CCD detector (CuKa radiation). The crystal-to-detector distance was 7 cm. Data were processed using the CrysAlis software package version 1.171.31.2 (Oxford diffraction) running on the Xcalibur PX control PC.

RESULTS AND DISCUSSIONS

Compressibility behavior of icosahedrite at high pressure

Synthetic icosahedral quasicrystals with the formula $Al_{63}Cu_{24}Fe_{13}$ (Bancel 1999) were used as starting materials for our *in situ* DAC experiments. An accurate textural and chemical analyses of the synthetic material showed minor amounts of (Cu, Fe)Al. The first set of experiments consisted of *in situ* powder angle-dispersive X-ray diffraction measurements on i-QC using

DACs up to ~50 GPa at room temperature. These experiments aimed to investigate the evolution of the icosahedral structure under pressure, the determination of the lattice parameter and the equation of state. A total of 50 diffraction patterns were collected during compression and decompression ramps. Figure 1 shows a characteristic spotty diffraction pattern constantly observed during our experiments and resulting from heterogeneous size of the crystallites.

Figure 2 shows the variation of the *d*-spacing for 7 known diffraction peaks with increasing pressure and after decompressing the sample to ambient pressure. The intensities of the peaks appear strongly affected by preferential orientation of the powder grains as also visible in Figure 1. However, the shift in *d*-spacing with increasing pressure can be observed for most of the peaks up to the target pressure. In addition, the peak broadening is also visible as the pressure increases. After the sample was decompressed to ambient pressure, peaks appeared still broadened in agreement with what observed by Sadoc et al. (1994) for i-$Al_{62}Cu_{25.5}Fe_{12.5}$. The results indicate that high pressure favors the disorder of the atoms in the QC, without causing drastic rearrangements of the structure itself.

We collected additional diffraction patterns at higher resolution by moving the detector at the maximum distance from the sample (~478 mm). This allowed us to investigate more accurately the icosahedral structure, in particular the behavior in the high *d*-spacing region that included peaks (12,16) at 5.53 Å and (8,4) at 8.94 Å, respectively. For the indexing notation see Lu et al. (2001). The collected diffraction patterns are shown in Figure S1; although limited at pressures up to ~36 GPa at room T, they clearly show the gradual broadening as pressure increases. Two additional peaks were also observed, with *d*-spacing of ~6 Å and 9.7 Å, respectively, never reported so far for i-AlCuFe, that could be indexed using the automated identification scheme described by Lu et al. (2001) as (24,15) and (6,3), respectively. Our *in situ* X-ray diffraction

measurements show that no peaks appear or disappear up to the target pressure of ~50 GPa, which excludes possible pressure-induced phase transformations, including amorphization, as in the case of i-AlLiCu (Itie et al. 1996). The observed peak-broadening with pressure can be interpreted as arising from the increasing atomic disorder perhaps due to residual stress while preserving the icosahedral structure within the investigated pressure range.

We determined the pressure dependence of the lattice parameter a_{6D} up to the maximum pressure of ~50 GPa (see Table S1 of Supporting Information). The parameter is defined as,

$$a_{6D} = d\sqrt{\frac{N + M\tau}{2(2+\tau)}} \qquad (1),$$

where d is the d-spacing in Å, N and M the Cahn indices for which the d-spacing is experimentally determined, and τ is the golden ratio, $(1+\sqrt{5})/2$ (Steurer and Deloudi 2009). The six-dimensional lattice parameter is shown to gradually decrease with increasing pressure (Fig. 3). The slightly scattered data at 24-32 GPa is likely due to the less accurate pressure determination caused by the overlap between the (111) peak of Ne and the (80, 128) peak of i-AlCuFe. However, the lattice parameter calculated from compression experiments is in good agreement with that calculated on decompression. The estimated reduction of the lattice parameter from the ambient pressure value of 12.64 Å is about 8%. In addition, our a_{6D} value at 5 GPa and room temperature is consistent with that determined by Stagno et al. (2014) at similar conditions. We conclude that the QC retains its icosahedral structure over the pressure range investigated. In addition, we point out that more specific experiments would be needed to claim the thermodynamic versus kinetic stability of icosahedrite. This note might be extended to most of the crystalline structures that have been investigated for decades using similar techniques, but

that in case of quasicrystals is of fundamental importance to understand their stability with respect to the possible alternative atomic configurations represented by amorphous and approximant phases (Tsai 2013). However, it remains still to be investigated whether these results confirm the stability of the i-QC under pressure or the transformation to a crystalline phase is too sluggish to be observed on the time scale of the experiment.

The zero pressure bulk modulus, K_0, and its pressure derivative K_0' were determined from the least-squares fit to several equation of state (EOS) models. We first discuss the fit to the first order Murnaghan EOS (Angel et al. 2014), which allows direct comparison with the results from previous studies in which the experimental data were treated using the same EOS model. This resulted in K_0 = 113.7(±2.9) and K_0' = 4.22(±0.22), respectively. It can be seen from Figure 4 that K_0 and K_0' obtained from our data are slightly lower than those obtained for $Al_{62}Cu_{25.5}Fe_{12.5}$ from previous authors using the same EOS, i.e., 139(±6) GPa and 2.7 (Sadoc et al. 1994), and 155(±10) GPa and 2 (Lefebvre et al. 1995). Our EOS parameters are also different from those determined for an approximant phase with composition $Al_{64}Cu_{24}Fe_{12}$ that is close to our synthetic i-QC, with K_0 and K_0' of 175(±16) GPa and 2.00 (Lefebvre et al. 1995). Such differences in the compressional behavior can be interpreted as due to either different composition of the QCs or distinct mechanical properties of the approximant (crystalline) phase. It should be kept in mind, however, that in previous studies in which DACs techniques were employed, silicon oil was used as a pressure medium, for which hydrostaticity is limited to very low pressure (Angel et al. 2007). Moreover, the previously suggested EOSs have been derived from data collected using energy-dispersive rather than angle-dispersive X-ray diffraction with the lattice parameter calculated using a different peak than the (8,4) used in this study without taking into consideration possible anisotropy of the material. Our experimental data were also fit

using either a third-order Birch-Murnaghan EOS [K_0 = 110.4(±2.9) and K_0' = 4.79(±0.28)] and a Vinet et al. EOS [K_0 = 109.4(±2.9) and K_0' = 5.06(±0.29)]. The new fitting models, although deviate slightly from the parameters obtained using a simple Murnaghan model, confirm the lower bulk modulus of synthetic icosahedrite with respect to the data currently available in literature. Finally, Figure 4 also shows the compressional behavior for pure *fcc*-Al, *fcc*-Cu (Dewaele et al. 2004) and *hcp*-Fe (Mao et al. 1990) plotted using the Vinet et al. and Birch-Murnaghan EOS models. For all these pure metals the structure has been reported to be stable for a wide pressure range > 100 GPa. As observed by Sadoc et al. (1994), the compressional behavior of our synthetic icosahedrite is much closer to that of pure Cu, although Al represents the main constituent. We expect, therefore, a similar compressional behavior for i-AlCuFe quasicrystals varying in compositions according to the phase diagram proposed by Bancel (1999).

Stability of the icosahedral symmetry at simultaneous high pressure and temperature

Recently, the conditions for the formation of natural i-AlCuFe have been constrained on the basis of accurate textural and chemical analyses of the coexisting mineral phases within the CV3-like chondritic grains of the Khatyrka meteorite (Hollister et al. 2014; MacPherson et al. 2013). The occurrence of rare alloys represented by the Al-Cu-Fe system along with the observation of melt droplets and phases such as stishovite and ahrensite have been referred to unusual petrological processes that likely occurred at simultaneous high pressures and temperatures generated by an impact shock. To shed light on the mechanisms of formation, a study of icosahedrite at high pressure and temperature could help to reach more definitive conclusions. A first study was done by Stagno et al. (2014) where the stability of synthetic

icosahedrite was observed *in situ* at 5 GPa up to ~1673 K above which the sample was found to melt incongruently and produce two solid crystalline phases: β-phase and cupalite. These experiments, although limited to demonstrate the kinetic stability of icosahedrite, provided the first evidence that pressure might act to stabilize the QC at *T* higher than 1300 K.

In situ high P-T laser heating system diamond-anvil cell experiments were conducted to further constrain the stability field of icosahedrite. The synthetic quasicrystalline powder was first compressed to ~42 GPa, then heated to ~ 1830 K while collecting X-ray diffraction patterns to monitor any possible transformation or melting (see details in the Experimental Methods session). The sample was then cooled down to 1000 K before being quenched. The results show that during heating at about 1560 K the intensity of most of the peaks decreases dramatically, and new peaks always belonging to QC appear at *d*-spacing between 1.8 and 2.0 Å (Fig. 5). Interestingly, during cooling of the sample at about 1500 K the main peaks re-appear and are visible even after quenching the sample to room *T*. No amorphization or phase transformation was evident, and the new peaks characteristic of the QC become visible as a result of a strong preferential orientation. However, with increasing *T* the loss of quasicrystallinity (i.e., formation of crystal approximants) via a reversible process cannot be excluded.

The result of the high *T* run performed at the same pressure on a different point of the sample is shown in Fig. S2 (Supporting Information). In this case the QC was heated up to ~2110 K and then quenched directly to room temperature. The results are similar to the previous experiment at 1600 K, where peaks characteristic of synthetic icosahedrite are present. At higher temperature, however, new unknown peaks appear that are preserved also after quenching the sample to room *T* suggesting that the i-QC might have decomposed irreversibly. *Ex situ* single crystal X-ray diffraction measurements on a micrometer-sized grain handpicked from the cell (see Fig. S3 of

Supporting Information) showed the 5-fold symmetry characteristic of i-QC. This result confirmed that the sample retained its structure, at least upon compression considering that it is difficult to establish whether or not the measured fragment was heated up to the target temperature.

To address the above questions, we performed additional quench experiments using multi-anvil technique to better understand the nature of the unknown peaks discussed above. Experiments were performed at 21 GPa and temperature between 1673-1993 K using icosahedral AlCuFe (≥99.9%) quasicrystalline powder with nominal composition of $Al_{65}Cu_{23}Fe_{12}$ previously characterized (Stagno et al. 2014).

SEM images using back-scattered electrons of the run products reveal the compositions and textures of the recovered material (Fig. 6). The run quenched from 1673 K consists of a single phase with composition $Al_{64.11(\pm0.66)}Cu_{24.70(\pm0.74)}Fe_{11.19(\pm0.22)}$, which is consistent with the starting composition of the synthetic QC. Several grains showed a patchy texture that we believe are due to the onset of melting of the QC. At about 1773 K the recovered sample shows the coexistence of β-phase ($Al_{64.73(\pm0.36)}Cu_{20.23(\pm0.91)}Fe_{15.04(\pm0.68)}$), Fe-rich cupalite ($Al_{48.77(\pm0.35)}Cu_{36.10(\pm0.93)}Fe_{15.13(\pm0.70)}$) and a phase identified by the patchy texture with composition $Al_{62.65(\pm0.89)}Cu_{33.52(\pm1.08)}Fe_{2.92(\pm0.27)}$ that can be interpreted either as a Fe-poor khatyrkite or a melt. Small grains of Al_2O_3 are also present and suggest possible oxidation of the material during the experiment. Finally, the recovered sample from 1973 K appears totally molten consisting of a Fe-rich liquid with composition $Al_{12.07(\pm0.50)}Cu_{21.34(\pm1.04)}Fe_{65.48(\pm0.73)}$ and with characteristic quench texture imposed by the presence of "skeletal" Al metal (Fig. 6d).

Results from quench experiments, therefore, would suggest 1) that the QC retains its stability at both high pressure and temperature and its icosahedral symmetry is also recoverable; 2) as temperature increases icosahedrite might melt congruently to, then, dissociate in a liquid with composition very similar to khatyrkite + β-phase + cupalite similarly to what reported by Stagno et al. (2014); 3) pure Al would be the first phase crystallizing from a liquid with icosahedrite-like composition.

IMPLICATIONS

Our results partially, but surprisingly, reproduce features observed in the Khatyrka meteorite in terms of phase assemblage (cupalite, β-phase, khatyrkite and pure Al) and texture, associated with the presence of icosahedrite. The coexistence of icosahedrite with a liquid having the same composition (i.e. congruent melting) than the ideal composition reported by Bancel (1999; i.e., $Al_{63}Cu_{24}Fe_{13}$) has been never reported at such high pressure and would imply the i-QC being, at least, kinetically stabilized by entropy at high pressure to the point where the melting temperature is approached without transformation to any approximant phase. This would agree with the fast cooling rate crystallization model proposed by Hollister et al. (Hollister et al. 2014; 10^2-10^3 °Cs^{-1}) from which the Al, Cu-rich assemblage formed. However, we point out that a similar mechanism of formation for icosahedrite appears unlikely as we assume here thermodynamic equilibrium between the QC and the liquid from which it forms. In fact, the coexistence of Al, Cu rich-phases with icosahedrite in the Khatyrka meteorite would suggest an initial high abundance of these elements, as confirmed by the finding of Al-rich Cu-bearing FeNi and sulfide phases in proximity of the QC. The finding of pure Al in our experiments is a further element of similarity with the natural assemblage (see Fig. 2 in Hollister et al. 2014) and can be

317 explained in light of its lower melting temperature with respect to Fe and Cu that would trigger
318 its mobilization by diffusion mechanisms and exsolution. The presence of khatyrkite in our
319 sample quenched at 1773 K with pure Al exsolved cannot be excluded and would represent a
320 further evidence of the high-temperature regime occurred during crystallization of these phases
321 even at pressures above 5 GPa within an extra-solar environment characterized by an unusual
322 abundance of Al.
323 To date, two hypotheses have been proposed (Hollister et al. 2014) to explain the origin of Al-
324 Cu-Fe alloys in the Khatyrka meteorite: 1) segregation from a silicate melt formed by an after-
325 impact heating event and enriched in Al and Cu previously diffused-out from Fe-Ni alloy, and
326 from which forsterite and diopside also could crystallize; 2) formation of Al-Cu metals during
327 nebular processes before the impact occurred with re-melting and re-solidification of these
328 alloys. Both scenarios appear as the result of multiple impact events that favored mechanisms
329 such as diffusion, solid-solid reactions and oxidation-reduction with a further common feature
330 represented by the initial high abundance of Cu and Al. It is, therefore, very unlikely that all
331 these processes can be explained based on our experimental results. On the other hand, our
332 experiments well reproduce the same phases observed in the meteoritic sample at higher
333 pressures and temperatures than those proposed by Hollister et al. (2014), where a pressure of 5
334 GPa and temperature of 1200 °C indicatively represent a lower-bound.

335 In conclusion, results from this study can be summarized as follows, 1) synthetic icosahedrite
336 was shown to retain its structure up to ~50 GPa at ambient temperature; 2) it was experimentally
337 demonstrated for the first time that pressure can stabilize the icosahedral Al-Cu-Fe quasicrystal
338 at very high temperature until it melts with no evidence of phase transitions; 3) congruent
339 melting of icosahedrite might be limited to a very narrow temperature interval beyond which Al,

Cu-rich phases would form. In addition, our results from quench experiments suggest that the bulk composition of the portion of solar nebula from which Khatyrka meteorite formed must have been much more enriched in Al and Cu than icosahedrite composition in case of single impact event followed by rapid solidification.

Based on our results the preservation of icosahedrite over cosmic time scales in a meteorite that formed at the early stage of the solar system results from its unexpected stability at high temperatures and pressures. Therefore, the presence of icosahedrite in other meteorites exposed to extreme conditions, but with similar bulk composition than Khatyrka, cannot be excluded.

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Captions

Figure 1. Representative powder X-ray diffraction pattern of i-$Al_{64}Cu_{23}Fe_{13}$ compressed at high pressure. Texture and contribution from single crystals are typical features of the collected patterns. The Debye-Scherrer rings were labeled as in case of QCs using the two-integer indexes by Janot (1994). The diffraction patterns were processed using Fit2D (Hammersley 1998) and Peakfit softwares.

Figure 2. Pressure dependence of the powder X-ray diffraction patterns of i-QC collected at room temperature in angle-dispersive mode (wavelength of 0.4246 Å). Filled circles indicate peaks of ruby (pressure marker), grey circles for Au (pressure marker), empty circles for Re (gasket) filled triangles for Ne (pressure medium). The diffraction peaks were indexed using Cahn indices (*N*, *M*) following the scheme proposed by Janot (1994; see also Steurer and Deloudi 2009).

Figure 3. Variation of the lattice parameter as function of pressure. Notes: yellow square, ambient pressure value (Bindi et al. 2011); black and white squares, lattice parameter determined respectively from compression and decompression experiments; gray squares, experiments at higher resolution.

Figure 4. Pressure-volume relations for i-$Al_{64}Cu_{23}Fe_{13}$ with experimental data (black squares) fitted using a Murnaghan EOS (dashed black line). Results from Birch-Murnaghan and Vinet et al. EOS fits are here omitted since both closely overlapped to the Murnaghan EOS fit. Uncertainties are within the symbol size. Our fit is compared with previous studies by Sadoc et al. (1994; gray line) and Lefbvre et al. (1995; blue line) both for icosahedral $Al_{62}Cu_{25.5}Fe_{12.5}$ and for one approximant phase with composition $Al_{64}Cu_{24}Fe_{12}$ (Lefbvre et al. 1995; yellow line). The

two curves obtained from these previous studies are extrapolated up to 52 GPa assuming that no structural phase transformation occurs. The EOS of pure Al, Cu (Dewaele et al. 2004) and Fe (Mao et al. 1990) are also reported with green, blue and brown, respectively.

Figure 5. Representative angle-dispersive (wavelength of 0.4133 Å) X-ray diffraction patterns for synthetic icosahedrite as function of temperature at ~ 42 GPa. Diffraction patterns were collected with 15s exposure time after keeping the sample at approximately constant *T* for 180s. Peaks are indexed as mentioned above. Filled black triangles indicate the (111) and (200) peaks of Ne pressure medium. a) Shown is the stability of i-QC during heating up to about 1830 K followed by slow cooling down to 1000 K before quench.

Figure 6. Back-scattered electron (BSE) images of the recovered sample from runs at 21 GPa. a) Run at 1673 K showing the presence of i-QC also confirmed by the five-fold symmetry in (b) using single crystal X-ray diffraction. (c) Recovered sample from 21 GPa and 1773 K and d) 1973 K, respectively.

Figures

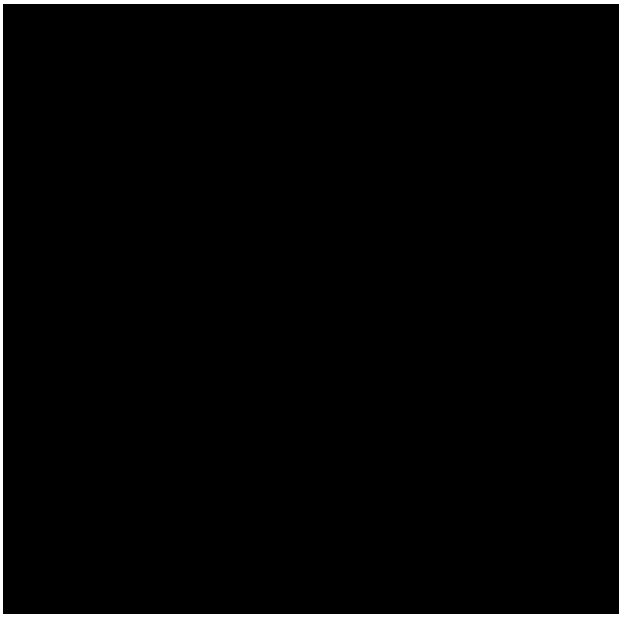


Figure 1

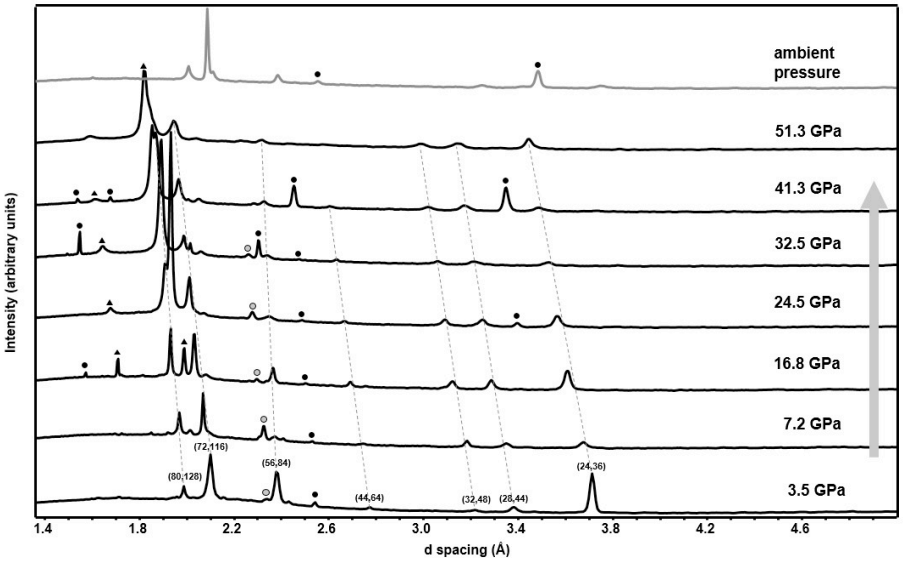
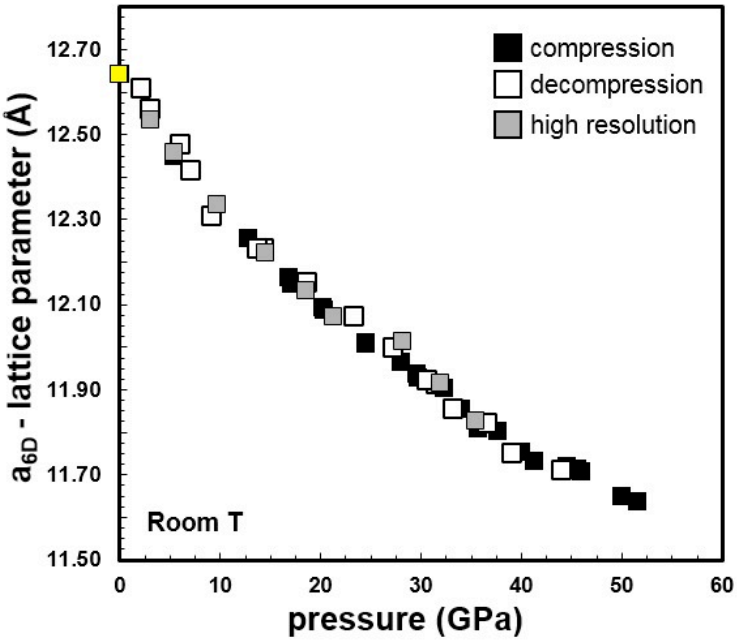


Figure 2



493

494 Figure 3

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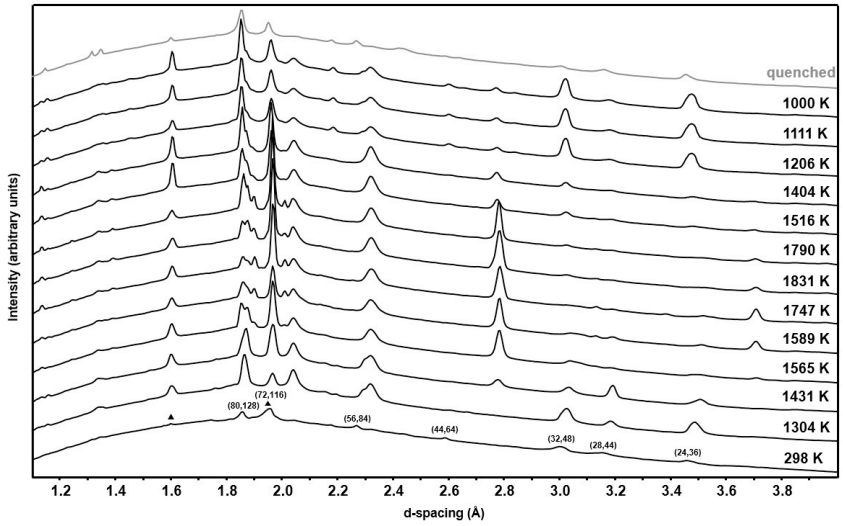
497 Figure 4



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499 Figure 5

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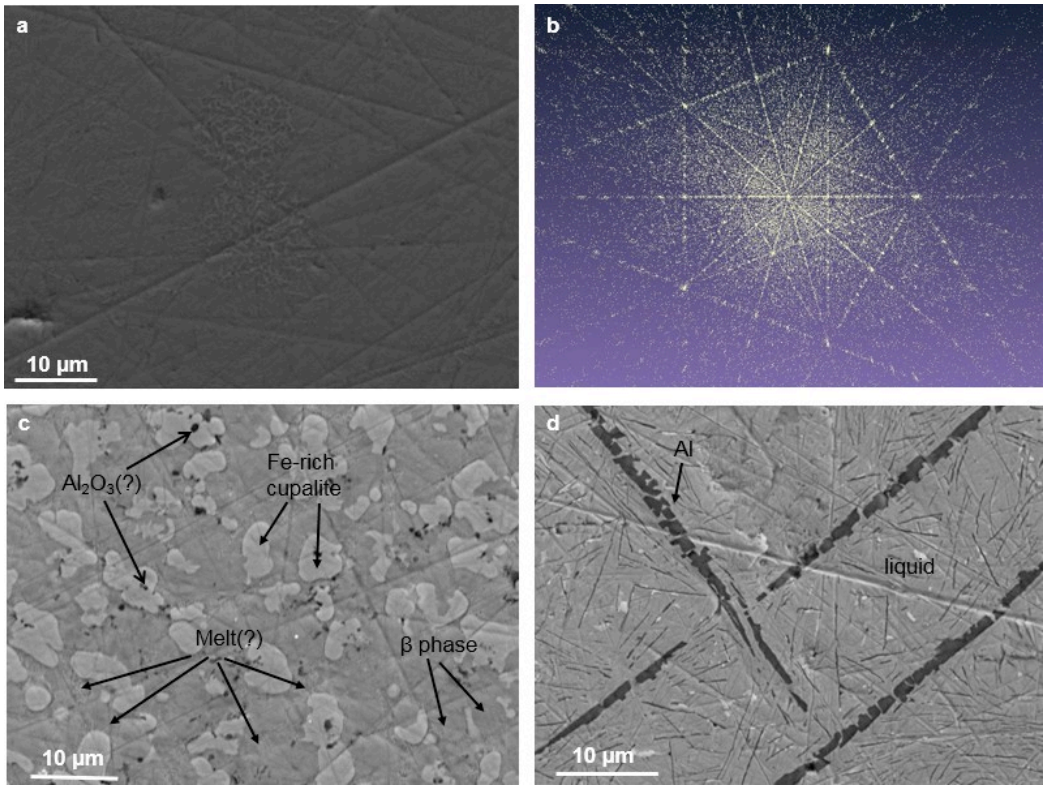

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504 Figure 6