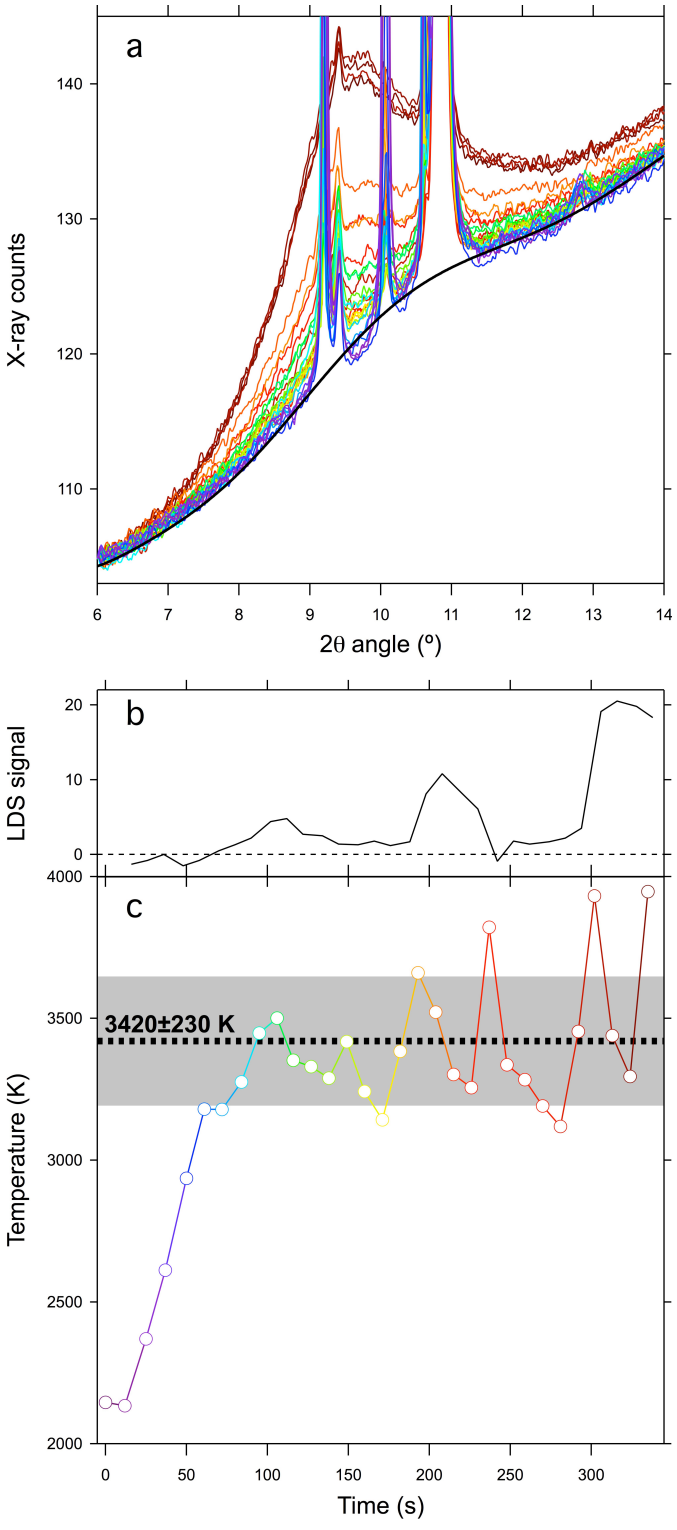
We were awarded 18 shifts on ID27 in April 2014 to study the high-pressure melting behaviour of a range of transition metals. During this time we studied Cu, Mo, Ti and V, extending our previous work on Ni (see report HS-4747). Some of the results of these experiments are presented below (§1). In addition, we performed a preliminary test of a new and exciting laser-heated diamond anvil cell (LH-DAC) methodology that we have been developing at the School of Earth Sciences, University of Bristol: full sample encapsulation. The results of that test are also briefly presented below (§2).



1. Melting curves of transition metals

As has been well documented, the melting curves of many transition metals are controversial, because the existing data from studies in the LH-DAC [e.g. 1] don't agree with the studies based on *ab initio* molecular dynamics [e.g. 2] and shock compression [e.g. 3]. The earlier LH-DAC studies used visual observation of melt motion as the melting criterion, which has been shown to underestimate melting temperatures in several materials including Fe and Ni [4,5,6]. It has been suggested that the earlier, off-line, studies may have misidentified sub-solidus recrystallization as melting. As with Ni, our new data on Mo suggest that the steeper melting curves reported in several theoretical and shock compression studies are in fact correct, and that the earlier LH-DAC studies underestimate the melting curve. For example, Fig. 1 shows a melting experiment performed during HS-1374 on Mo at 30 GPa which clearly indicates the onset of melting at 3420±230 K both from the appearance of diffuse scattering and a simultaneous plateau in the temperature vs. time function (which is proportional to laser power. This is over 400 K higher than the temperature determined previously at this pressure using visual observation [1]. It has been observed that the melting curves of some transition metals are not controversial: for example, in the case of Cu, *ab*

Figure 1 | *In situ* melting of Mo at 30 GPa. (a) XRD patterns showing diffuse scattering, colour coded as a function of time from the start of laser heating. A constant y-offset is applied to each pattern such that they are equal at 2θ = 6° (b) magnitude of the diffuse scattering signal as a function of time at 2θ = 9.8° relative to the baseline of the pattern collected immediately after temperature quench (the black line in a). (c) power versus temperature data, colour coded as a function of time as in (a) such that both can be directly correlated. The dashed line and grey bar represent the melting temperature and its associated uncertainty based on the position of the temperature plateau. Note that LDS occurs at the onset of the plateau.

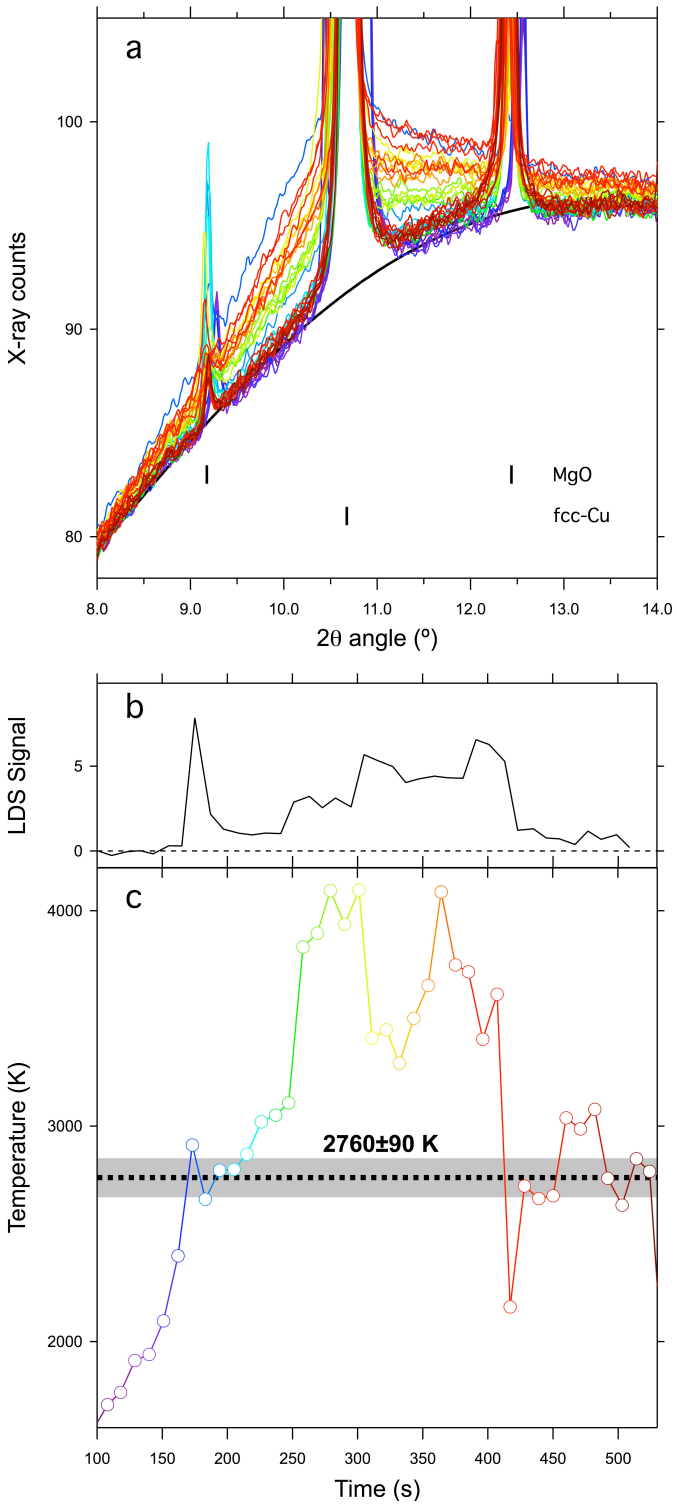


Figure 2 | *In situ* melting of Cu at 37 GPa. Labeling and formatting as in Fig. 1.

initio methods and visual observation in the LH-DAC agree [7]. Fig. 2 shows the results of a melting experiment performed on Cu at 37 GPa, also during HS-1374. As expected, a short plateau coincides with the onset of strong diffuse scattering from the liquid at 2760 ± 90K, which is within error of both the previous off-line LH-DAC and *ab initio* studies. One of many outstanding questions still under investigation as part of this study is why these different methods agree for some metals (such as Cu) but not others (such as Mo). One interesting observation that may be relevant here is that many transition metals, including Mo, are carbide formers at ambient pressure, whereas Cu is not. It is apparent from the XRD data collected during HS-1374 that this situation remains the same at high pressures; even at 3000 K, Cu shows no evidence of carbide formation despite the proximity of the sample to the diamond anvils. Future work on this study includes: 1. Completing the analysis of the XRD data, including experiments on Ti and V, 2. Performing additional off-line melting experiments, 3. Perform *ex situ* analysis of the textures and chemistry of the samples with electron micro-beam methods, after sectioning them using a focussed ion beam and 4. Attempting to determine liquid structure and density by extracting the diffuse scattering signal from our XRD data and fitting its radial distribution function.

The data from this study are still being processed.

2. Sample encapsulation in the LH-DAC

LH-DAC experiments, though of great utility to experimental petrology, nevertheless suffer from several key limitations. Firstly, temperature gradients are often considerable, leading to Soret or saturation gradient diffusion that can seriously compromise the bulk sample composition and the accuracy of phase relations and partitioning studies. Secondly, in the case of silicate samples relevant to Earth's mantle, the choice of pressure media is very limited, as most (including oxides and halides) will react with the sample, again compromising results. This means that materials such as MgO, which is desirable because of its very melting point, cannot be safely used. This is especially problematic in simple systems such as $MgO\text{-}SiO_2$ (MS) and $CaO\text{-}MgO\text{-}SiO_2$ (CMS) where solidus and liquidus temperatures are very high. A common strategy to solve this problem is to mix the sample with an absorber, such as Pt, and then use the sample without the absorber as the pressure medium. However, this makes phase-out boundaries impossible to detect, because even at temperatures above such a boundary, there will always

be a location along the temperature gradient between the sample surface and the diamond anvil where that phase remains stable. Thirdly, many systems of interest (such as MS and CMS) do not absorb Nd:YAG laser light with $\lambda = 1$ μm. Though CO_2 lasers can be used ($\lambda = 10$ μm), these are less ubiquitous, more expensive and require special coated reflective optics while absorbers mixed with the sample can lead to serious temperature gradients. To circumvent these issues, we have developed, at the School of Earth Sciences, University of Bristol, a novel micro-fabrication technique in which a silicate sample is fully encapsulated with a high-melting point transition metal, such as Re. First, the sample powder is placed on top of a bow-tie shaped, 20 μm thick, resistively heated Re-filament, with the narrow, central part containing 30-40 laser-drilled holes with a diameter of 20 μm. The molten powder fills the holes and quenches to glass. Next, the filament, with its glass-filled chambers, is polished and then ion milled to a thickness of ~10 μm. Afterwards, both sides of the filament are sputter coated with a thin (~100 nm) layer of a conductive and oxygen-active metal such as Mo in order to enhance adhesion between the glass and the much thicker (~1 μm) layer of Re-metal subsequently applied via electroplating. Finally, the filament is annealed at ~600 K in an evacuated silica tube containing Fe wool to reduce any remaining fluid from the electroplating process. The finished capsules (~80 μm in diameter and ~15 μm thick) are then laser cut from the filament. The encapsulant acts as the laser absorber, so that iron-free samples can be heated, allows essentially any material to be used as the pressure medium because it is physically separated from the sample, and greatly reduces temperature gradients within the sample. The capsule can also be used as the pressure marker at room temperature (and high temperature, if its thermal equation of state is known). Essentially, this method marries many of the advantages of the piston-cylinder or multi-anvil press with the huge P-T range of the LH-DAC. During HS-1374 we successfully tested one such Re-encapsulated sample of model MORB composition using MgO as the pressure medium, in order to be able to compare our results with the diffraction data of [8]. Some of the results of this experiment are presented in Fig. 3. Before heating (a) the sample clearly consists of amorphous glass (the broad feature at $2\theta = 10°$) and Re metal, with peaks form the MgO pressure medium also apparent. During heating (b) at 2500 K, the Re peaks are still present, suggesting that the capsule is intact and the glass has reacted to form an assemblage of Mg-perovskite, Ca-perovskite, stishovite and the calcium ferrite (CF) structured phase, as expected. After quenching from the liquidus (c) the assemblage is essentially the same, except for two prominent peaks at $2\theta = 8°$ that are as yet un-indexed.

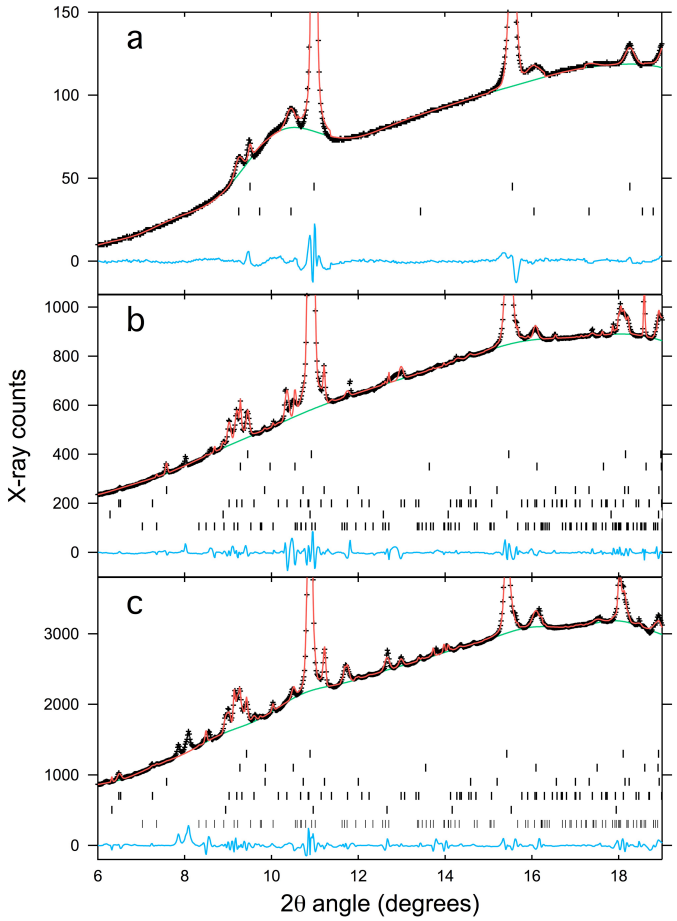


Figure 3 | Le Bail fits (red lines), backgrounds (green dashed lines) and residuals (blue lines) for XRD data (pluses) from a Re encapsulated MORB sample before laser heating (a), *in situ* at 2500 K (b) and after temperature quench (c). The post heating pressure was 50 GPa. The tick marks represent reflections of, from top to bottom, MgO, Re, Mg-perovskite, stishovite, Ca-perovskite and the calcium-ferrite structured phase.

A technical paper describing this new methodology is currently in preparation.

References: [1] Errandonea D et al. (2001) *Phys Rev B*,

63:132104. [2] Cazorla C et al. (2007) *J. Chem Phys*, **126**:194502. [3] Nguyen JH et al. (2014) *Phys Rev B*, **89**:174109. [4] Anzellini, S. et al. (2013) Science 340:464-466. [5] Lord OT et al. (2014) *Phys Earth Planet Inter*, **233**:13-23. [6] Lord OT et al. (submitted) *Earth Planet Sci Lett*. [7] Ross M et al. (2007) *Phys Rev B*, **76**:184117. [8] Hirose K et al. (2005) *Earth Planet Sci Lett*, **237**:239-251.