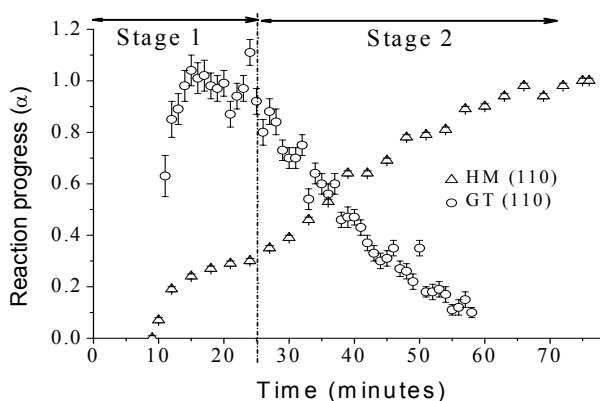


## The effect of lead on the kinetics and mechanisms for the formation of hematite from ferrihydrite

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The crystallisation of hematite (HM) from 2-line ferrihydrite (FH) in the presence of lead was studied under alkaline condition at temperature between 160 and 240°C using synchrotron-based, *in situ* energy dispersive X-ray diffraction. The data showed that HM formed via a two-stage crystallisation process with goethite (GT) as an intermediate phase (Fig.1). In the first stage, HM and GT both formed from FH, whereas in the second stage HM crystallised from GT.



**Figure 1:** Reaction progress ( $\alpha$ ) for the FH to GT and HM reaction at 180°C.

The time-resolved data was fitted with the Johnson-Mehl-Avrami-Kolmogorov model (JMAK) [1] to extract rate constants and induction times. From the Arrhenius plots the activation energies of nucleation ( $E_a(\text{nuc.})$ ) and crystallisation ( $E_a(\text{cryst.})$ ) of HM in the first stage were 15.8 and 67.1 kJ/mol respectively, while the  $E_a(\text{cryst.})$  in the second stage was 73.3 kJ/mol. Combining with previous studies [2, 3] an aqueous-aided 2D transformation mechanism is proposed for the HM crystallisation

When compared with the crystallization of HM from pure FH under equivalent conditions [3] the data showed that the presence of lead (20 mg Pb/ g FH) reduced the reaction rate by about one order of magnitude.

[1] Avrami (1939) *J. Chem. Phys.* **8**, 212-224. [2] Bao & Koch, (1999) *GCA* **63**, 599-613. [3] Shaw *et al.* (2005) *Am. Min.* **90**, 1852-1860.

## Xenolith glasses: A key to deciphering mantle processes?

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Silicate glasses, common in mantle xenoliths from both continental and oceanic settings, have been variously interpreted in relation to processes that occur in the upper mantle or during transport to the surface. We studied here anhydrous and hydrous lherzolites from a continental setting (Massif Central, France) in which cryptic and modal metasomatism has been evidenced [1, 2], in order to test the potentiality of glasses for identifying the nature of the metasomatizing agent. Usually, minerals rather than glasses are used to study metasomatic processes, as the small size of the glasses makes the analysis difficult. However, the EMP procedure developed in our laboratory allows to analyze trace elements (Sr, La, Ce, Nd, Zr, Ti, Y) at the micro scale [3].

Fresh glasses occur as pockets in reaction zones between minerals or as thin veinlets along grain boundaries. The glass composition, which falls within that of world-wide mantle xenolith glasses, varies between the different xenoliths or within one single xenolith. In the hydrous samples, glassy pockets of clinopyroxene, olivine, spinel ( $\pm$  plagioclase) and formerly volatile-filled bubbles are frequently associated with amphibole. The amphibole breakdown exerts a major control on the glass composition, but an additional component is required in particular to account for the alkali budget. On discriminating major element plots [4], glasses from hydrous samples fall both within the alkali silicate- and carbonatite- related metasomatism fields (depending on the xenolith or on the glass settings in one xenolith), while glasses from anhydrous samples are related to a carbonatite metasomatism. However, the trace element signature may be in contradiction with the major element information.

Thus, caution is required in using the glass geochemical signature for elucidating mantle processes, and further studies of effects of melt-rock ratios on the composition of the metasomatic agent are needed.

[1] Wagner & Deloule (2007) *Geochim. Cosmochim. Acta* **71**, 4279-7296. [2] Bouhedja *et al.* (2002) 12th Goldschmidt Conf, *Geochim. Cosmochim. Acta.* A96. [3] Fialin *et al.* (1999) *Am. Mineral.* **84**, 70-77. [4] Coltorti *et al.* (2000) *Earth Planet. Sci. Letters* **183**, 303-320.