

CLOSED SYSTEM OXYGEN ISOTOPE REDISTRIBUTION IN IGNEOUS CAIs UPON SPINEL DISSOLUTION. J. Aléon¹, ¹IMPMC UMR 7590, Museum National d'Histoire Naturelle, 61 rue Buffon, 75005 Paris, France (jerome.aleon@mnhn.fr).

Introduction: The mineralogical control on O isotopes in igneous Ca- Al-rich inclusions (CAIs) from chondritic meteorites has been puzzling ever since the discovery of large ¹⁶O excesses in CAI minerals from Allende [1]. Among the four major CAI minerals, spinel and clinopyroxene (cpx) are typically ¹⁶O-rich, whereas melilite and anorthite are typically ¹⁶O-poor. A range of compositions are sometimes observed for pyroxene, melilite and anorthite but spinel is systematically ¹⁶O-rich with a $\Delta^{17}\text{O}$ value at -24‰. This distribution is not compatible with a simple isotopic evolution during CAI melt crystallization, nor quantitatively with a secondary isotope exchange by solid state diffusion, nor with a late isotopic exchange during hydrothermal fluid circulations, nor with aggregation of condensate minerals formed in different gas reservoirs. Solid state diffusion and aggregation of condensates are possible explanations for some type A CAIs [2,3] and hydrothermal fluid circulations probably explain isotopic variations in small and fine-grained CAIs from chondrites metasomatized/metamorphosed to some extent [4,5]. However none of these mechanisms explain satisfactorily the isotopic distribution in coarse-grained type B CAIs. Two recent studies [6,7] demonstrated that cpx in type B CAIs became ¹⁶O-enriched during its magmatic crystallization, requiring two episodes of isotopic change during CAI crystallization with first a depletion in ¹⁶O and second a return to the initial ¹⁶O-rich composition. Both studies concluded that the two isotopic exchanges could be explained by equilibration with nebular gaseous reservoirs of differing composition. However this interpretation fails to explain the O isotopic composition of FUN (Fractionated with isotopic anomalies of Unknown Nuclear origin) CAIs, in which the mineralogical control on the ¹⁶O excess is nevertheless similar to that of unfractionated CAIs. Here I compile O isotopic compositions and TiO₂ content of cpx of several igneous CAIs representative of compact type A, type B and FUN CAIs and investigate whether a single process can explain their compositions.

Samples: *Allende USNM 3529-Z* is a classical unfractionated type B1 CAI studied in detail for O isotopes. The $\Delta^{17}\text{O}$ -TiO₂ relationship in cpx is well established [6]

Allende CMS-1 is a new FUN CAI [8], for which O isotopes and TiO₂ content are both available in cpx. CMS-1 is strongly mass fractionated in both spinel and cpx.

Allende STP-1 is a type B2 FUN CAI documented for O isotopes [9] but coupled O isotopes - TiO₂ content in cpx are not available. However its intermediate degree of mass fractionation is important for the comparison between FUN and non-FUN CAIs

Allende 7R-19-1 is a compact type A CAI with several coarse-grained igneously zoned cpx [10], intermediate in that respect between type A and type B CAIs. Coupled $\Delta^{17}\text{O}$ -TiO₂ contents are only available in two portions of pyroxene grains.

Efremovka E101,3 is a classical compact type A CAIs with only small amounts of very TiO₂-rich, ¹⁶O-poor cpx interstitial between melilite crystals [11].

Model rationale: In FUN CAIs, the O isotopic composition of cpx and spinel define two trends, which intersect at highly mass fractionated and ¹⁶O-rich composition. Being specific to individual CAIs, these intercepts point toward an indigenous component at the origin of the ¹⁶O-rich cpx rather than equilibration with a common unfractionated ¹⁶O-rich gas. Interestingly, a back-reaction of early crystallized spinel with partial melt has been evidenced in CMAS melts and suspected during crystallization of type B CAIs [e.g. 12]. I used mass balance considerations to investigate whether spinel dissolution is consistent with the observed compositions of the 5 above CAIs. Spinel is assumed to dissolve by increments in the melt and crystallization of cpx is assumed to freeze the composition of the melt at each step owing to the slow self-diffusivity of O in cpx. Based on linear TiO₂ profiles in single sectors of igneously zoned cpx in 3529-Z, the TiO₂ content is assumed to decrease linearly during crystallization of cpx. Initial and final $\Delta^{17}\text{O}$ values, extent of mass fractionation and Ti content are dictated by the composition of the samples. The only free parameter of the model is f_M the fraction of O atoms from the melt ($1-f_M$ being the fraction of O atoms from spinel), which takes into account the stoichiometry of the spinel dissolution reaction and is adjusted for each CAI.

Results and discussion: The $\Delta^{17}\text{O}$ -TiO₂ relationship shows that cpx is initially Ti-rich and ¹⁶O-depleted and becomes ¹⁶O-rich and Ti-poor as crystallization progresses in all the considered CAIs. This notably includes the CMS-1 FUN CAI, where the composition of cpx evolves toward that of mass fractionated spinel rather than evolving from it. The $\Delta^{17}\text{O}$ values drop rapidly initially and reach the spinel value more progressively. Although much less data are available, Type A CAIs show a similar evolution but

represent a separated trend rather than extending the type B CAI trend. In all CAIs these trends are nicely reproduced by the expected evolution of the partial melt upon spinel dissolution (Fig. 1). When the three O isotopes are considered, the composition of cpx is achieved after a few dissolution steps during which the composition of the melt matches that of anorthite (3529-Z) or melilite (STP-1). In FUN CAIs the mixing trend is reproduced by dissolving a fraction of the most mass fractionated spinel ranging from 1 in CMS-1 to 0.5 in STP-1. As the composition of cpx approaches rapidly that of spinel, it is rapidly dominated by ^{16}O -rich cpx, as classically observed. A ^{16}O -poor composition is only preserved in the very first increments of cpx crystallization, in the crystal cores.

The f_M values required to fit the composition of cpx in these CAIs range from 0.6 in CMS-1 to 0.9 in the type A CAIs and is 0.8 in the type B CAIs. Interestingly these values are roughly correlated with the amount of spinel in the considered CAIs as deduced independently from electron microscopy or bulk rocks analysis: CMS-1 is very rich in spinel whereas the two type A CAIs contain much less spinel.

The match between the observed compositions and the dissolution of spinel requires that the CAI partial melts did not equilibrate with the nebular gas during cpx crystallization to allow individual CAI to preserve the isotopic signature of an indigenous component. Because physical isolation from the gas is not realistic, this implies a chemical isolation, that is insufficient O partial pressure in the gas or a cooling rate too high for significant exchange. Contrary to common assumptions, igneous CAIs did not equilibrate with the nebular gas during a significant fraction of their cooling history.

The isotopic composition of spinel in their interior and Wark-Lovering rims, testifies that CAI sampled a ^{16}O -rich gas at the beginning and end of their formation (Fig. 2). To account for the ^{16}O -depletion in melilite and at the beginning of anorthite and cpx crystallization, an open-system stage with equilibration of the partial melt with a ^{16}O -poor gas is required. In all CAIs, this ^{16}O -depletion is related with the crystallization of melilite and possibly partial remelting, i.e. at $T \sim 1400\text{-}1500^\circ\text{C}$. It further requires sufficiently high partial pressures of O in the gas. Interestingly, the shock wave model [13] provides thermal histories that are potentially consistent with this scenario.

Conclusion: Simple mass balance calculations show that the dissolution of early crystallized ^{16}O -rich spinel, expected from experimental petrology, into a partial melt that previously experienced a ^{16}O -depletion is a simple explanation for the mineralogical control of the O isotopic anomaly in all igneous CAIs

and deserves to be investigated in more details. More experimental work is needed to unravel the conditions of this dissolution and its implication for the distribution of O isotopes in the protoplanetary disk.

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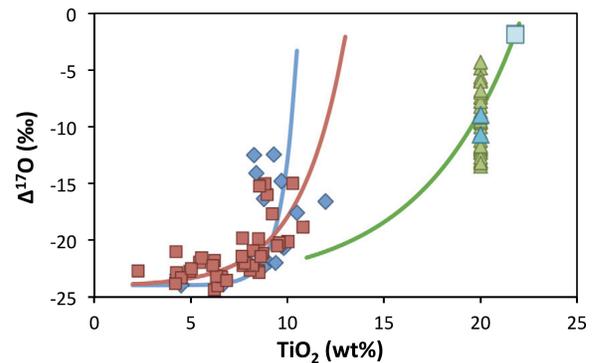


Fig. 1 Oxygen isotopic evolution of cpx in 3529-Z (red); CMS-1 (blue); in the profiles from 7R-19-1 (green triangles, averages are teal) and E101,3 (light blue square). Curves: spinel dissolution model. Modified from [14].

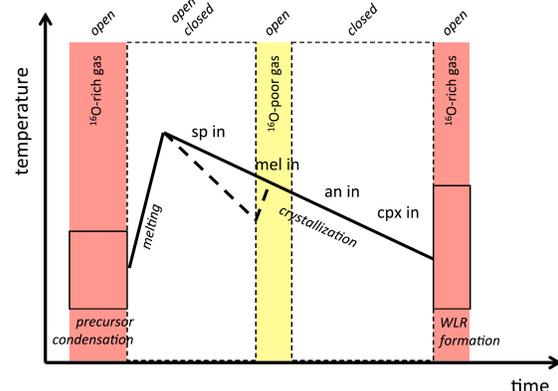


Fig. 2 Schematic description of the isotopic-thermal history of igneous CAIs. Plain and dashed lines are differing thermal histories matching O isotopes. Modified from [14].