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Significance of monophase fluid inclusions in minerals

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Abstract — Monophase fluid inclusions in minerals were reinterpreted by Arnold in 1986. For him, they are an indication of crystal growth under surface P-T conditions. The three points in support of his contention are considered. Except very special situations, the great bulk of published reports of monophase fluid inclusions are still best interpreted as evidence of metastability.

Signification des inclusions fluides monophasées dans les minéraux

Résumé — *Les inclusions fluides monophasées dans les minéraux sont réinterprétées par Arnold en* 1986. *Pour ce dernier, elles sont l'indice d'une croissance du cristal dans des conditions P-T de surface. Les trois points de l'argumentation d'Arnold sont considérés et critiqués. Sauf cas très particulier, la grande majorité des inclusions fluides monophasées étudiées dans la littérature sont interprétées rigoureusement en termes de métastabilité.*

Version Française abrégée — Dans un article récent, Arnold [1] déclare que la « contraction de l'eau liquide durant son refroidissement permet *toujours* la création mécanique d'une bulle de vapeur ». Pour cette raison, Arnold propose une réinterprétation de centaines de travaux sur les inclusions fluides monophasées ([6], [7]) dans les minéraux des roches. Si cette réinterprétation était correcte, elle aurait un impact majeur sur les modèles métallogéniques et sur les procédures de prospection minérale.

Les points importants de l'argumentation d'Arnold [1] sont les suivants :

1. L'analogie avec le rétrécissement du liquide du thermomètre.
2. L'état métastable suppose une énergie libre de surface considérablement augmentée et très hautement hypothétique.
3. La déformation irréversible des parois de l'inclusion par variation de la température.

En contraste, Roedder ([7], [8]) maintient qu'une inclusion fluide de liquide sans bulle de vapeur peut exister dans des conditions métastables, même dans la nature ou au laboratoire, dans le champ P-T particulier où la vapeur est une phase stable, sous des pressions *négatives* sans nucléation de bulle.

Les trois points de l'argumentation d'Arnold [1] sont reconsidérés :

1. Par référence aux travaux de Berthelot [2] et de Richards et Trevena [4], l'analogie avec le thermomètre est réfutée.
2. Un effet métastable implique effectivement par définition une énergie libre plus élevée que l'état stable. Mais une telle énergie libre plus élevée n'exclut pas l'existence de cet état : en effet, la persistance d'un liquide dans un état métastable, sans nucléation de bulle de vapeur, est extrêmement commune dans la nature et les expériences de laboratoire et résulte d'une variété de phénomènes étudiés ailleurs ([5], [7], [8]). La meilleure preuve de l'existence de tels états métastables est l'apparition instantanée d'une bulle de vapeur à une température de quelques degrés (dT) en dessous de la température d'homogénéisation originelle (Th). L'interprétation est donnée par l'extension de l'isochore sous la courbe L+V, dans un diagramme P-T. La figure donne les isochores pour deux inclusions fluides A et A′, piégées à 95 bars et à 50 et 30°C.
3. L'argument qui invoque la déformation des parois des inclusions est vrai dans les cas extrêmes cités par Arnold [1]. Mais il est inapproprié pour les faibles variations de

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Note présentée par Georges MILLOT.

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température utilisées par les « tenants de la théorie de la métastabilité ». La figure montre que, plus le refroidissement sous Th est fort, plus la nucléation d'une bulle de vapeur est rapide.

Quelques autres observations sont données en addition aux indications théoriques et expérimentales précédentes, qui confirment cette conclusion.

La conclusion finale d'Arnold [1] est que « la coexistence d'inclusions aqueuses monophasées et biphasées contemporaines est l'indice d'une croissance dans une solution de basse température et chargée de bulles de gaz ». Ceci peut effectivement être vrai dans quelques situations naturelles particulières, dans des minéraux de basse température. Mais nous maintenons, comme la grande majorité des études de la littérature, l'existence d'inclusions monophasées et biphasées simultanément piégées, qui sont correctement interprétées comme une évidence de la métastabilité des inclusions monophasées.

Arnold [1], p. 459, states that the "contraction of liquid water during its natural cooling *always* permits a mechanical appearance of vapour bubble" [emphasis added]. For this reason, Arnold says that Roedder [7] is incorrect in his interpretation of some monophase fluid inclusions, which Roedder believed to result from the continued existence of metastable, "stretched" liquids at pressures less than the equilibrium vapor pressure of the liquid at the given temperature. As a result, Arnold believes that monophase inclusions, which occur in the minerals of various ore deposits, must have been formed at surface P-T conditions. Such a reinterpretation of the significance of the literally hundreds of reports of monophase inclusions (e. g., [6]) would, if valid, have a major impact on many metallogenetic models, as well as on mineral exploration procedures.

Arnold [1] makes the following three points in support of his contention:

1. A fluid inclusion is analogous to a thermometer; when cooled, the liquid must shrink.

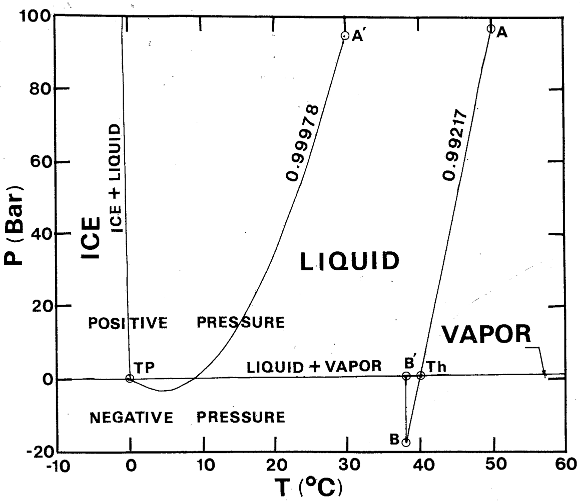
2. Metastable "stretched" fluids, if they were assumed to exist, would have an increased and "highly hypothetical" surface free energy.

3. "The proponents of the theory of metastability emphasize that these inclusions generally produce the 'expected bubble' when they are cooled or heated" (p. 460); Arnold then shows that both of these procedures will result in the formation of a bubble from irreversible (outward) deformation of the walls of the inclusion, thus increasing the volume.

In contrast, Roedder [7]; *see* also [8], Chapter 10, Metastability, believes that a fluid inclusion consisting of liquid but without a vapor bubble can exist, metastably, in a particular P-T field where vapor is the stable phase, under *negative* pressures, without nucleation of a bubble. The original bubble-free state can be arrived at by various P-T paths. Thus an original small bubble can be eliminated by expansion of ice on freezing [8], *Fig*. 10-1. The most commonly encountered situation, however, involves cooling a previously homogeneous inclusion. It is of no consequence whether the inclusion was originally trapped as a homogeneous fluid or was homogenized by heating in the laboratory; the principles are the same.

Let us now consider Arnold's three points.

POINT ONE. — The thermometer analogy, as drawn, is simply not applicable to the situation under consideration. A thermometer normally consists of a volume of fluid *and vapor* in a rigid tube. On cooling, the liquid shrinks and the volume of vapor



Pressure-temperature phase diagram for the system H_2O from data of [3]. The isochores for two densities are plotted to true scale, but dP/dT for the two-phase, (liquid + vapor) curve has been exaggerated 3-fold to help show the existence of a very thin stable vapor field between the (liquid + vapor) curve and zero pressure.

Diagramme de phase P.T pour le système H_2O à partir des données de [3]. *Les isochores pour les deux densités ont été reportées en vraie valeur, mais la courbe dP/dT pour les deux phases* (*liquide + vapeur*) *a été exagérée d'un facteur* 3 *pour montrer l'existence d'un très étroit champ de stabilité de la vapeur entre la courbe* (*liquide + vapeur*) *et la pression zéro.*

increases, exactly as does a two-phase fluid inclusion. For the present situation, the analogy to a thermometer would be apt only if the liquid in the thermometer had been heated until it *filled* the tube and eliminated the vapor phase. Subsequent cooling may not result in nucleation of the vapor phase. This *full* thermometer (and the monophase inclusions) is an exact analogy of the famous glass tubes made by M. Berthelot [2] in a classic study of "stretched", metastable water. Richards and Trevena [4] describe the application of a modern Berthelot tube in which the change of pressure (or tension) in the enclosed liquid can be measured directly by an internal strain-gauge pressure transducer. With this device they determined the metastable extensions of the isochores for water in the 20-50°C range from positive pressure to 30 atm negative pressure.

POINT TWO. — Here, Arnold is correct in that a metastable state, by definition, does indeed involve a higher free energy than the stable state. Such higher free energy does not, however, preclude the existence of the metastable state. The persistence of liquids in a metastable state, from the failure to nucleate a vapor bubble, is extremely common in both nature and the laboratory, and results in a variety of fascinating phenomena that need not be reviewed here (*see* references in [5], [7], and [8]). By far the most poignant and apropos evidence for the existence of such metastable, stretched fluids in inclusions lies in the standard and simple observation, by every fluid inclusion worker, that on cooling previously homogenized fluid inclusions, the vapor bubble appears at a temperature generally some degrees (ΔT) below that at which it originally homogenized (Th). Further, the appearance is visually *instantaneous*. The value of ΔT for any single inclusion varies somewhat from run to run, with the vagaries of nucleation statistics, whereas repeat runs on Th produce experimentally identical data.

The normal interpretation by most fluid inclusion workers is that once the bubble has been eliminated, cooling resulted in following the metastable extension of the appropriate isochore down below the L+V curve on a P-T plot, into a region of metastable, stretched fluid (*Fig.*). As soon as a vapor phase nucleates, it expands instantly to eliminate the negative pressure and put the inclusion system back on the stable L+V curve. The excursion into the field of metastable liquids at first is in an area of positive pressures (*see* also [8], *Fig.* 10-1), but with further cooling, this metastable extension quickly moves into the area of *negative* pressures (tension). This is particularly true for inclusions formed at low temperatures, because the width (in terms of pressure) of the field of stable vapor on a P-T plot in this range is extremely small (*Fig.*).

Figure shows the isochores for two inclusions of pure water, A and A′, trapped at 50 and 30°C, respectively, both at about 95 bars pressure. On cooling, inclusion A follows the isochore for density 0.992 17 g/cm^3 to the L+V curve at Th (40°C), where it should nucleate a vapor phase at a pressure of 0.073 8 bar. If vapor nucleation does not occur, on slight further cooling (only 0.008 5°C, since dP/dT at Th=40°C is 8.715 bar/°C), zero pressure will be reached. Further cooling will continue to follow the metastable extension of the isochore, Th-B, until nucleation occurs. Thus if cooled to 38°C, the inclusion would have an internal (negative) pressure of −16.95 bars. If nucleation occurs at B, the inclusion would return instantly to the L+V curve at B′, and P=0.06 bar. On rewarming, this bubble would disappear at Th. Inclusion A′, with a higher density, has a theoretical Th of about 9°C; the metastable extension of this isochore shows a reversal due to the maximum in the density of liquid water at about 4°C.

POINT 3. — This is also quite true as stated; if a monophase inclusion is cooled or heated to the extremes described by Arnold, it will indeed become permanently deformed and hence will develop a new vapor bubble. Unfortunately, however, the point is inappropriate, as it amounts to a case of reductio ad absurdum. The "cooling or heating" described by "the proponents of the theory of metastability" refers to much smaller temperature changes. The probability of nucleation of a vapor bubble in a given time increases as the tensile stress on the liquid increases. The further the inclusion is taken along a metastable extension, the larger the free energy increase, and the more likely is the nucleation of vapor. Thus in Figure, the greater the cooling below Th, the shorter the time for nucleation of vapor. Similarly, heating a frozen inclusion that has lost the vapor phase can take the inclusion down the metastable extension of the ice+liquid curve to larger values of negative pressure, perhaps to as much as −1,000 atm [5].

In addition to the theoretical and experimental evidence described above, several other observations should be mentioned:

1. In mixtures of one- and two-phase inclusions, as found, only the larger inclusions are two-phase.
2. Laboratory operations can result in the nucleation of a vapor bubble in some inclusions that were one-phase as found, and if the treatment was not so drastic as to cause permanent deformation, Th for these new bubbles will be the same as Th for those originally with bubbles as found.
3. The higher the Th for the two-phase inclusions, the less likely it will be to find one-phase inclusions and the smaller they must be. As is expected for metastable systems, specific numerical limitations are not applicable, but many inclusion studies show that such small one-phase inclusions become increasingly rare as Th of the two-phase inclusions increases above about 70°C, but there are examples involving Th even >100°C.

Arnold's final conclusion [1], p. 461 is that "the coexistence of contemporaneous one- and two-phase aqueous inclusions is therefore an indication of crystal growth in a very low temperature solution charged with gas bubbles". This could indeed be true of some special natural situations, but we believe that the great bulk of the published reports of one-phase inclusions coexisting along with presumably coeval two-phase inclusions are still best interpreted as evidence of metastability.

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