

An overview on current fluid-inclusion research and applications 当前流体包裹体研究和应用概况*

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Abstract This paper provides an overview of some of the more important developments in fluid-inclusion research and applications in recent years, including fluid-inclusion petrography, PVTX studies, and analytical techniques. In fluid-inclusion petrography, the introduction of the concept of 'fluid-inclusion assemblage' has been a major advance. In PVTX studies, the use of synthetic fluid inclusions and hydrothermal diamond-anvil cells has greatly contributed to the characterization of the phase behaviour of geologically relevant fluid systems. Various analytical methods are being developed and refined rapidly, with the Laser-Raman and LA-ICP-MS techniques being particularly useful for volatile and solute analyses, respectively. Ore deposit research has been and will continue to be the main field of application of fluid inclusions. However, fluid inclusions have been increasingly applied to other fields of earth science, especially in petroleum geology and the study of magmatic and earth interior processes.

Key words Fluid inclusions, FIA; PVTX; Fluid-inclusion analysis; fluid-inclusion application

摘 要 本文概要总结近年来流体包裹体研究和应用的发展情况,包括流体包裹体岩相学,PVTX 研究,分析技术和应用等四个方面。岩相学方面的主要进展反映在“流体包裹体组合”概念的提出和应用。在 PVTX 研究方面,人工包裹体和热液金刚石压腔的应用极大地促进了我们对地质流体体系相特征的了解。各种分析技术不断涌现或改进,其中以 Laser-Raman 对气体成分和 LA-ICP-MS 对溶质成分的分析尤其有用。流体包裹体的应用领域一直以矿床学研究为主,当前和今后一段时间内仍将如此。但是,流体包裹体在地球科学的其它领域,尤其是石油地质以及岩浆和地球内部过程的研究等方面,正得到越来越多的应用。

关键词 流体包裹体; 流体包裹体组合; PVTX; 流体包裹体分析; 流体包裹体应用

中图分类号 P589.1; P591.2; P611.13; P618.13

Introduction

The research on and applications of fluid inclusions have progressed tremendously over the last two decades. This is reflected by the increasing number of papers on fluid-inclusion studies in earth-science journals. For example, more than 450 papers dealing with fluid inclusions have appeared in *Geochimica et Cosmochimica Acta* and *Chemical*

Geology since the 1980's, including several special issues devoted to the subject. The percentage of papers containing fluid-inclusion studies in *Economic Geology* increased steadily from 5% in 1975 to 27% in 2000 (Fig. 1). This trend is not surprising given that fluids are involved in most geologic processes, and fluid inclusions are the only samples of the actual paleo-fluids. With the continuous improvement of analytical techniques, fluid inclusions will continue to become

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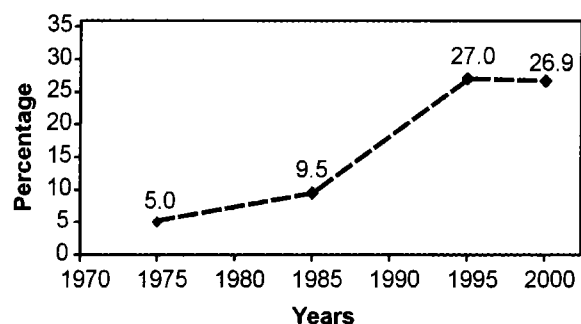


Fig. 1 A diagram showing the increase in the percentage of papers with fluid-inclusion studies in *Economic Geology* from the year of 1975 to 2000.

- an indispensable tool in studying virtually every geologic process where they were formed and preserved.
- This paper gives an overview of some of the more important developments in fluid-inclusion research and applications in recent years. They are summarized in four topics: (1) petrography, (2) *PVTX* studies, (3) analytical techniques, and (4) applications. The paper is not meant to be a comprehensive review of all the developments in fluid-inclusion studies, but aims to provide the readers with an overall picture of the current status of the subject and some key references. Other recent reviews on fluid-inclusion research and applications may be found in De Vivo and Frezzotti (1994), Roedder and Bodnar (1997), Brown (1998), Shepherd and Rankin (1998), Lu and Guo (2000), and a special volume of *Lithos* (volume 55, 2001).

Fluid-inclusion petrography

Fluid-inclusion petrography is the basis of any fluid-inclusion study. It has been increasingly emphasized that a few fluid-inclusion data with detailed petrographic constraints are worth more than thousands of poorly constrained data. The purpose of fluid-inclusion petrography is to establish the relative timing of the entrapment of fluid inclusions with respect to their host mineral, and to provide the basis for evaluating the meaning and validity of fluid-inclusion data. The validation of fluid-inclusion data has been drawing more and more attention.

The classification of fluid inclusions into primary, secondary, and pseudosecondary continues to be widely used, with the discrimination criteria of Roedder (1984) being commonly cited. However, these terminologies are commonly abused. It is not uncommon that some fluid inclusions are claimed to be 'primary' without any petrographic description. It should be emphasized that the 'primary-pseudosecondary-secondary' terminologies are interpretative, and not descriptive. For example, the four types of occurrences of fluid inclusions shown in Figure 2 may all be interpreted as primary. However, in the cases of Figures 2B, C and D, the possibility of secondary or pseudosecondary origin cannot be ruled out, and it is wrong to simply claim these inclusions as primary.

Probably the single most important advance in fluid-inclusion petrography in recent years is the development of

the concept of 'fluid-inclusion assemblage' or 'FIA' (Goldstein and Reynolds, 1994). An FIA is a group of fluid inclusions that were entrapped at the same time and that are petrographically distinguishable (*e. g.*, all the inclusions along the same growth zones in a single crystal or all inclusions along a single healed fracture) (Goldstein and Reynolds, 1994). It differs from a 'population' in that the latter is less restrictive in terms of contemporaneity. It is also different from the term 'generation', which implies broad contemporaneity and does not emphasize spatial continuity. For example, a generation of fluid inclusions may include all primary fluid inclusions in all crystals that were formed at the same period of time, whereas an FIA refers to one specific group of fluid inclusions in one specific growth zone in one specific crystal. A particularly useful tool in FIA studies is the Scanning Electron Microscope-Cathodoluminescence (SEM-CL) and the optical high-power CL-microscope which can reveal detailed microtextures in quartz (Kerkhof and Hein, 2001).

The concept of FIA is very useful in avoiding the bias of fluid-inclusion data and in evaluating the validity of the data, especially in discriminating the so-called 'three devils of fluid inclusions': necking, heterogeneous trapping, and stretching. In principle, if fluid inclusions in one FIA were entrapped from a homogeneous fluid phase and were not modified after trapping, their microthermometric attributes should be the same. In practice, if the variation of homogenization temperatures of fluid inclusions within an FIA is less than 15°C, the FIA may be considered representing homogeneous trapping without significant post-trapping modification (Goldstein and Reynolds, 1994; Goldstein, 2001). In this case, the average of the microthermometric data of all the fluid inclusions within the FIA may be used to represent the FIA, and only one datum (*i. e.*, the average) should be included in statistics (*e. g.*, a histogram) (Fig. 3A). Conversely, if the variation of homogenization temperatures of fluid inclusions within an FIA is larger than 15°C, the FIA may have been subject to post-trapping modification (necking or stretching) or may represent heterogeneous trapping. In the former case, the microthermometric data are unusable (Fig. 3B), and in the latter case, the minimum homogenization temperature should be used to represent the FIA (Fig. 3C).

PVTX studies

Knowledge of the *PVTX* properties of fluids is essential for understanding the phase behaviour of fluid inclusions in laboratory conditions and for estimating the P-T conditions at entrapment. There are generally two approaches for *PVTX* studies: experiments and theoretical modeling, the latter being partly based on data obtained from the experiments.

The results of experiments and theoretical modeling of common geological fluid systems prior to the early 1980's have been reviewed by Burruss (1981), Crawford (1981), Holloway (1981), and Roedder (1984). Major progress has been made since then, largely due to the application of synthetic fluid inclusions starting in the mid 1980's (Stern

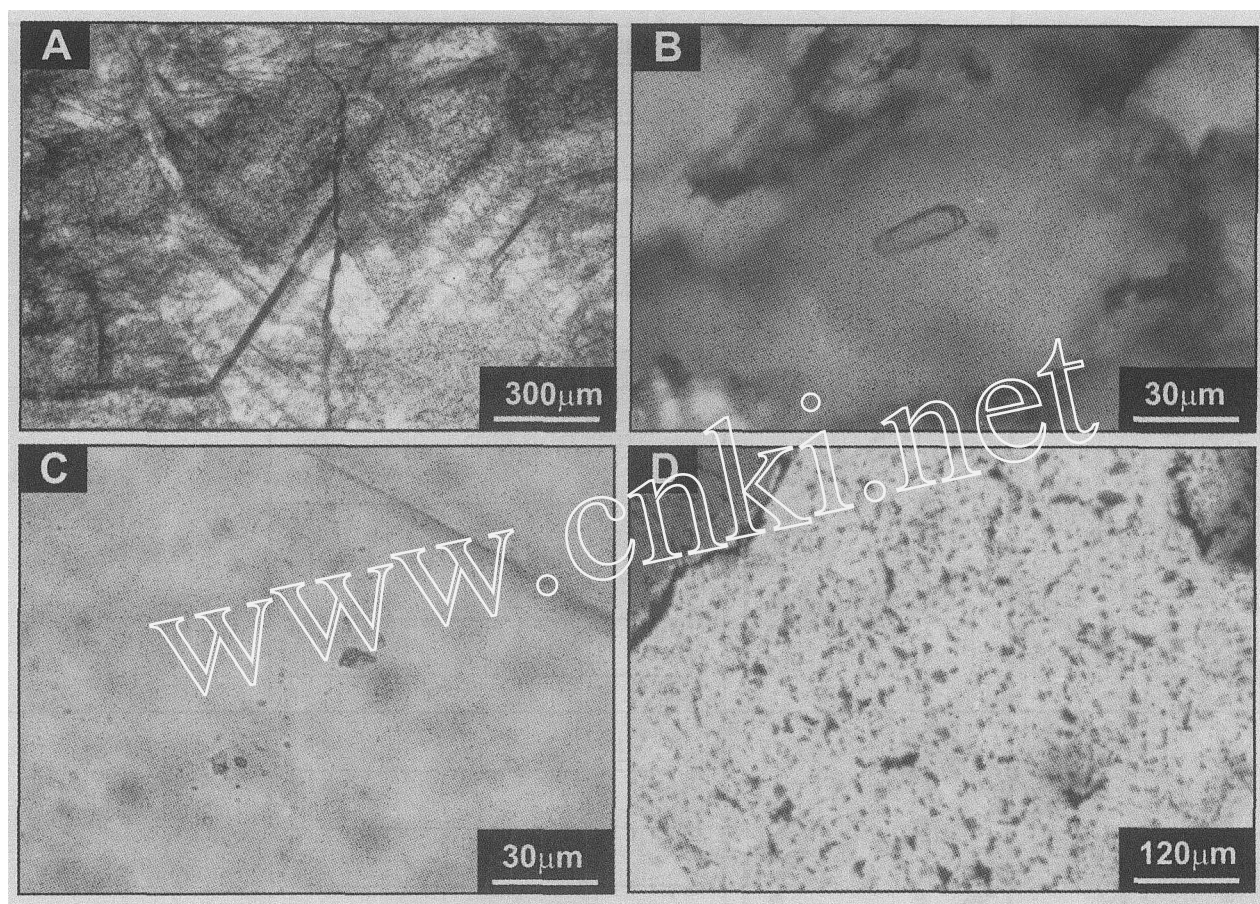


Fig. 2 Photomicrographs showing various occurrences of fluid inclusions that may be interpreted as primary inclusions. (A) Fluid inclusions occurring in growth zones in ankerite. (B) An isolated fluid inclusion in sphalerite. (C) Clusters of fluid inclusions in quartz. (D) Randomly distributed fluid inclusions in quartz. Although these fluid inclusions are likely primary, the possibility that some of them are secondary or pseudosecondary cannot be ruled out. Therefore, it is more informative and less subjective to describe these fluid inclusions by their modes of occurrence instead of simply calling them primary fluid inclusions.

and Bodnar, 1984; Bodnar and Sterner, 1985), and in part due to the application of the hydrothermal diamond-anvil cell since the early 1990's (Chou *et al.*, 1994). In addition to the progress in experimental methods, the development and widespread application of computer software for modeling PVTX properties, in particular Flincor (Brown, 1989) and MacFlincor (Brown and Hagemann, 1994), have played a significant role in the application of fluid inclusions to geological studies.

More recent reviews on the PVTX properties of geological fluids include papers in De Vivo and Frezzotti (1994), Brown (1998), and papers in a special volume of *Lithos* (volume 55, 2001). Table 1 lists some of the more important references on common geological fluid systems. Most experimental work earlier than the 1980's are not listed, but they can be found in the selected references, some of which are review papers. Some of the systems (*e.g.*, H_2O - NaCl - CO_2) are better studied than others (*e.g.*, H_2O - NaCl - MgCl_2 and H_2S -bearing systems).

While new experiments will continue to provide increasingly refined data sets for various aqueous $\pm$ volatile systems over extended conditions, increased attention has been paid recently to hydrocarbon systems. Some initial

experiments have been carried out on aqueous-petroleum systems using synthetic inclusions (*e.g.*, Teinturier *et al.*, 2002). The PVTX modeling of petroleum fluid inclusions has been the subject of a number of recent studies (see Munz, 2001), and computer programs such as PIT (Thiery *et al.*, 2000) have been developed.

Analytical techniques

Analytical techniques represent the fastest growing field in fluid-inclusion research. The evolution of the existing techniques and the development of new techniques are reflected in review papers published at different times (*e.g.*, Roedder, 1984, 1990; Boiron and Dubessy, 1994; Shepherd and Rankin, 1998). It is not the intention of this paper to review the various techniques, but a summary of them is given in Table 2, with one or two representative references being listed for each method.

Despite the development of sophisticated analytical methods, microthermometry remains the indispensable method for fluid-inclusion studies. Infrared microthermometry for fluid inclusions in opaque minerals,

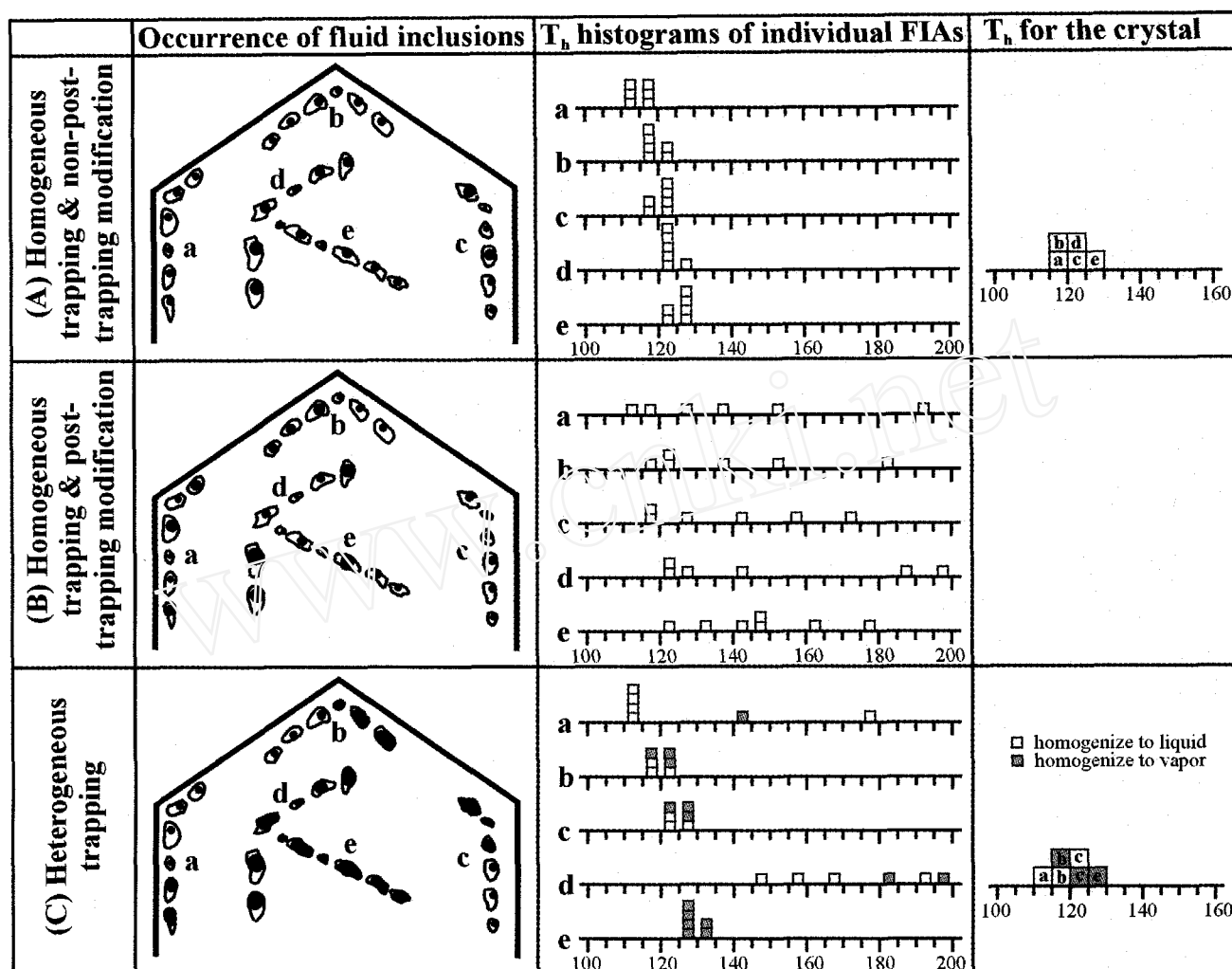


Fig. 3 A schematic representation of three situations of fluid inclusion assemblage (FIA) and data treatment. (A) The homogenization temperatures (T_h) of fluid inclusions within individual FIAs are convergent. Only one value (the average) per FIA is included in the histogram for the crystal. (B) The T_h values of individual FIAs are divergent (variation more than 15°C), indicating post-trapping modification. The microthermometric data are unreliable, and should not be included in statistics. (C) Some fluid inclusions homogenize into the liquid phase, and some homogenize into the vapour phase, suggesting the existence of two immiscible fluid phases. The large variation of T_h values results from heterogeneous trapping. If there is a convergence at the lower end of the T_h spectrum for individual FIAs (a, b, c, and e), the minimum (represent the trapping temperature) should be included in statistics. If there is no convergence at the lower end of the T_h spectrum for individual FIAs (d), even the minimum values may have been affected by heterogeneous trapping, and should not be included in statistics.

first used in the late 1980's (Campbell and Robinson-Cook, 1987), has received renewed attention in recent years, with application to common sulfides such as pyrite (Luders and Ziemann, 1999). Furthermore, commercial instruments are now available.

In volatile analysis, although bulk analysis by gas mass spectrometry (MS) and gas chromatography (GC) is still widely used, the Laser Raman microspectrometric technique has become a standard method for quantitatively analyzing volatile compositions of individual fluid inclusions (Burke, 2001). One of the current research efforts in Raman microspectrometry is to quantify trace amounts of gases such as methane in aqueous fluid inclusions (Dubessy *et al.*, 2001). Gas chromatography (GC) and gas chromatography-

mass spectrometry (GC-MS) have been increasingly applied to analysis of hydrocarbon fluid inclusions (George *et al.*, 1997).

In solute analysis, although conventional bulk analysis of leachate is still the main method, the laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has been increasingly used to obtain quantitative data for individual fluid inclusions (Gunther *et al.*, 1998). This technique is one of the most hotly studied fields of fluid-inclusion analysis, and will probably become a key method for analyzing solute composition of single fluid inclusions, as Laser-Raman does for volatiles. The scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) analysis of fluid-inclusion decrepitates or broken frozen

Table 1 Selected references on PVTX studies of fluid-inclusion related chemical systems

Systems	Experiments	Theoretical Modeling
H ₂ O	20, 26, 79	16, 26, 31, 40, 41, 45, 46, 54, 63, 64
CO ₂	1, 26, 68	13, 16, 26, 31, 44, 46, 54, 57, 64, 72, 75
CH ₄	2, 26	26, 31, 39, 44, 46, 48, 54, 64, 73
H ₂ O-NaCl	8, 11, 42, 55, 59, 82	7, 9, 10, 14, 15, 17, 19, 69, 82
H ₂ O-KCl	42, 71, 82	42, 69, 71
H ₂ O-CaCl ₂	36, 59, 60, 61, 82, 83	69, 82
H ₂ O-MgCl ₂	37, 80	34, 69
H ₂ O-CO ₂	23, 27, 70	4, 5, 6, 14, 16, 13, 23, 24, 25, 27, 33, 46, 54
H ₂ O-CH ₄	21, 27, 56	1, 24, 27, 29, 35, 48, 81
CO ₂ -CH ₄	27	15, 27, 32, 43, 44, 48, 50, 52, 53, 73, 74
H ₂ O-NaCl-KCl	42, 71, 82	12, 17, 19, 71, 82
H ₂ O-NaCl-CaCl ₂	36, 59, 61, 76, 82	69, 78, 82
H ₂ O-NaCl-MgCl ₂	37	34, 69
H ₂ O-NaCl-CO ₂	23, 35, 38, 58, 65, 66, 67	6, 4, 14, 17, 22, 23, 24, 29, 33
H ₂ O-NaCl-CH ₄	56	4, 24, 28
H ₂ O-CO ₂ -CH ₄	84	4, 24, 27, 30, 48, 47
H ₂ O-CO ₂ -CH ₄ -NaCl	58	4, 24
N ₂ -bearing systems	3, 58	4, 24, 30, 31, 32, 33, 44, 46, 49, 50, 52, 53, 64, 73, 74
H ₂ S-bearing systems	62, 77	24, 31, 51, 85

[1] Angus *et al.*, 1976; [2] Angus *et al.*, 1978; [3] Angus *et al.*, 1979; [4] Bakker 1999; [5] Bakker and Diamond 2000; [6] Bakker *et al.*, 1996; [7] Bischoff, 1991; [8] Bischoff *et al.*, 1986; [9] Bischoff and Pitzer, 1989; [10] Bodnar, 1993; [11] Bodnar *et al.*, 1985; [12] Bodnar *et al.*, 1988; [13] Bottinga and Richet, 1981; [14] Bower and Helgeson, 1983; [15] Brodholt, 1998; [16] Brown and Lamb, 1986; [17] Brown and Lamb, 1989; [18] Burruss, 1981; [19] Chou, 1987; [20] Chou *et al.*, 1998; [21] Chou *et al.*, 2001; [22] Darling, 1991; [23] Diamond, 1992; [24] Diamond, 1994; [25] Diamond 2001; [26] Duan *et al.*, 1992a; [27] Duan *et al.*, 1992b; [28] Duan *et al.*, 1992c; [29] Duan *et al.*, 1995; [30] Duan *et al.*, 2000; [31] Dubessy, 1994; [32] Dubessy and Thiery, 1994; [33] Dubessy *et al.*, 1992; [34] Dubois and Marignac, 1997; [35] Frantz *et al.*, 1992; [36] Gibbard and Fong, 1975; [37] Gibbard and Gossmann, 1974; [38] Gibert *et al.*, 1998; [39] Grevel, 1990; [40] Haar *et al.*, 1984; [41] Halbach and Chatterjee, 1982; [42] Hall *et al.*, 1988; [43] Herskowitz and Kisch, 1984; [44] Heyen *et al.*, 1982; [45] Hill, 1990; [46] Holloway, 1981; [47] Huizenga 2001; [48] Jacobs and Kerrick, 1981; [49] Jacobsen *et al.*, 1986; [50] Kerkhof, 1990; [51] Kerkhof and Hein, 1992; [52] Kerkhof and Thiery, 1994; [53] Kerkhof and Thiery 2001; [54] Kerrick and Jacobs, 1981; [55] Knight and Bodnar, 1989; [56] Lamb *et al.*, 1996; [57] Mader and Berman, 1991; [58] Murphy and Roberts, 1997; [59] Oakes *et al.*, 1990a; [60] Oakes *et al.*, 1994; [61] Oakes *et al.*, 1990b; [62] Prausnitz *et al.*, 1986; [63] Saul and Wagner, 1989; [64] Saxena and Fei, 1987; [65] Schmidt and Bodnar 2000; [66] Schmidt *et al.*, 1995; [67] Shmulovich and Graham, 1999; [68] Shmulovich and Shmonov, 1975; [69] Spenser *et al.*, 1990; [70] Sterner and Bodnar, 1991; [71] Sterner *et al.*, 1988; [72] Sterner and Pitzer, 1994; [73] Swanenberg, 1979; [74] Thiery *et al.*, 1994; [75] Touret and Bottinga, 1979; [76] Vanko *et al.*, 1988; [77] Vargaftik, 1975; [78] Williams-Jones and Samson, 1990; [79] Withers *et al.*, 2000; [80] Wolf *et al.*, 1986; [81] Zhang, 1997; [82] Zhang and Frantz, 1987; [83] Zhang and Frantz, 1989; [84] Zhang and Frantz, 1992; [85] Touray and Guilhaumou, 1984.

inclusions (cryogenic method) is a fast and economic way of obtaining semi-quantitative data of major elements of individual fluid inclusions, and the use of environmental scanning electron microscope (ESEM) has produced accurate quantitative data (Timofeeff *et al.*, 2000). The synchrotron X-ray fluorescence (SXRF) microprobe is a highly sensitive non-destructive method for detecting trace elements in individual fluid inclusions (Menez *et al.*, 2002). With the development of the third-generation synchrotron radiation sources, this technique will potentially become one of the most important methods of solute analysis.

Stable isotopes, especially hydrogen and oxygen isotopes, of fluid inclusions have long been used as tracers of

geological fluids (Kesler *et al.*, 1997). Halogens and noble gases and their isotopes in fluid inclusions are increasingly studied (Villa, 2001). Rb-Sr isotopes of fluid inclusions have been used in determining the age of sphalerite from Mississippi Valley-type deposits (Christensen *et al.*, 1995). The major problem with all these methods is the same for any bulk analysis method: the results commonly reflect mixtures of multiple generations of fluid inclusions. The solution of this problem lies in the development of new mass-spectrometry technique that requires a very small sample so that different generations of fluid inclusions can be analyzed separately.

Table 2 Summary of fluid inclusion analysis techniques and selected references

Single inclusion techniques	Reference
<u>Non-destructive methods</u>	
<u>Volatile analysis</u>	
Microthermometry (MT): Estimation of compositional systems and density of gases.	[20]
Infrared Microthermometry (IRMT): Study of fluid inclusions in some opaque minerals.	[15]
Laser Raman Microspectroscopy (LR): Semi- to quantitative analysis for gas mixtures.	[5], [8]
Fourier Transform Infrared Microspectroscopy (FTIR): Compliment. to Raman. Hydrocarbons.	[16]
UV Fluorescence Microspectroscopy (UVF): Liquid hydrocarbons. Estimation of API values.	[26]
<u>Solute analysis</u>	
Microthermometry (MT): Estimation of compositional systems. Salinity $\pm$ ion ratios.	[12], [20]
Infrared Microthermometry (IRMT): Study of fluid inclusions in some opaque minerals.	[15]
Synchrotron X-ray Fluorescence (SXRF): Trace element analysis. Depth of FI critical.	[17]
Proton Induced X-ray Emission analysis (PIXE): Similar to SXRF but lower sensitivity.	[1], [22]
Proton Induced Gamma-ray Emission analysis (PIGE): Complement. to PIXE for light elements.	[1]
<u>Other analysis</u>	
Transmission electron microscopy (TEM): Nano-scale structures and FI shapes.	[29]
Confocal Laser Scanning Microscopy (CLSM): 3D imaging of FI and bubble, esp. petroleum.	[2]
<u>Destructive methods</u>	
<u>Volatile analysis</u>	
Laser-Induced Mass Analyzer (LIMA): Potentially powerful, yet to be developed.	[21]
<u>Solute analysis</u>	
Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS): Trace elements.	[11]
LA-ICP Atomic Emission Spectrometry (LA-ICP-AES): Similar to LA-ICP-MS, cation only.	[19]
Laser Ablation Atomic Emission Spectrometry (LA-AES): Similar to LA-ICP-AES, simple.	[9]
Secondary Ion Mass Spectrometry (SIMS): Trace and light elements, near-surface FIs, melt FIs.	[7]
Cryogenic Scanning Electron Microscope Energy Dispersive Spectrometry (C-SEM-EDS):	[27]
Decrepitation SEM-EDS (D-SEM-EDS): Semiquantitative analysis of major elements.	[13]
Electron Microprobe Analysis (EMPA): Major and minor elements, mainly for melt FIs.	[31]
<u>Bulk sample techniques</u>	
<u>Non-destructive methods</u>	
<u>Solute analysis</u>	
Instrumental Neutron Activation Analysis (INAA): Host mineral free of target elements.	[30]
<u>Destructive methods</u>	
<u>Volatile analysis</u>	
Gas Mass spectrometry (MS): Quantitative analysis of various volatiles except high HC.	[18]
Gas Chromatography (GC): Quantitative analysis of various volatiles including high HC	[24]
Gas Chromatography Mass Spectrometry (GC-MS): High hydrocarbons including biomarkers.	[10]
<u>Solute analysis</u>	
Ion Chromatography (IC): Best for anions, some cations. May be integrated with GC.	[6]
ICP-AES and ICP-MS: Major and trace cations, some anions.	[3]
<u>Isotopes</u>	
H and O isotopes: Tracing the origin of water.	[14], [25]
Rb-Sr isotopes: Dating sphalerite from Mississippi Valley-type deposits.	[23]
Noble gas and isotopes: Tracing the origin of volatiles.	[28]
Cl isotopes: Tracing the origin of salinity.	[4]

[1] Anderson *et al.*, 1989; [2] Aplin *et al.*, 1999; [3] Banks *et al.*, 1994; [4] Banks *et al.*, 2000; [5] Burke, 2001; [6] Der Channer *et al.*, 1999; [7] Deloule *et al.*, 1995; [8] Dubessy *et al.*, 2001; [9] Fabre *et al.*, 1999; [10] George, 1997; [11] Gunther *et al.*, 1998; [12] Haynes, 1985; [13] Haynes *et al.*, 1988; [14] Kesler *et al.*, 1997; [15] Luders and Ziemann, 1999; [16] Pironon *et al.*, 2001; [17] Menez *et al.*, 2002; [18] Moore *et al.*, 2001; [19] Ramsey *et al.*, 1992; [20] Roedder, 1984; [21] Roedder, 1990; [22] Ryan *et al.*, 1993; [23] Pethke and Diamond, 1995; [24] Salvi and Williams-Jones, 1997; [25] Simon, 2001; [26] Stasiuk and Snowdon, 1997; [27] Timofeeff *et al.*, 2000; [28] Villa, 2001; [29] Viti and Frezzotti, 2001; [30] Wilkinson, 1990; [31] Belkin *et al.*, 1998.

Application of fluid inclusions

The trends in the application of fluid inclusions in recent years may be divided into three categories: (1) the increasing application to additional branches of earth science, (2) the continued dominant application in ore-deposit research, and (3) the rapidly increasing application in petroleum geology

and the study of magmatic and earth interior processes.

The widespread application of fluid inclusions in earth sciences is a logical consequence of the fact that fluids are involved in most geologic processes, and fluid inclusions are the only samples of the actual ancient fluids. Thus, fluid inclusions have been applied to such variable fields as the study of the upper mantle processes (Anderson and Neumann, 2001), deep fluid in subduction zones (Scambelluri and Philippot, 2001), magmatic processes (Li,

1994; Frezzotti, 2001), the composition of ancient seawater (Kovalevich *et al.*, 1998), paleoseismic processes (Boullier and Robert, 1992), and the occurrence and nature of ancient micro-organisms (Vreeland *et al.*, 2000; Hazen and Roedder, 2001).

The research of ore deposits, especially hydrothermal ore deposits (Roedder and Bodnar, 1997; Wilkinson, 2001), continues to be the most important field of application of fluid inclusions. In most studies, fluid-inclusion data serve as a major constraint on models of ore genesis, especially on fluid compositional systems and temperature-pressure conditions. In some cases, fluid inclusions provided key evidence of a mineralization process and resulted in a breakthrough of genetic models. For example, the study of the fractionation of trace elements between coexisting immiscible brine and vapour inclusions in magmatic mineralization systems using the LA-ICP-MS method revealed that Au, As, Cu and Sb may be strongly partitioned into the vapour phase (Heinrich *et al.*, 1999). This may explain the genetic relationship between some Cu-Au porphyry deposits and epithermal deposits, and represents a major breakthrough in this field. In another example, the study of melt inclusions in volcanic rocks associated with a modern seafloor hydrothermal system revealed that magmatic fluids may be a major contributor for the metals in VMS deposits (Yang and Scott, 1996), which was merely a speculation before the report of the evidence from fluid inclusions. A final example is the determination of the ages of some Mississippi Valley-type deposits by the Rb-Sr dating method of fluid inclusions in sphalerite, which provided important constraints on the relationship between orogenies and MVT mineralization (Nakai *et al.*, 1990).

Hydrocarbon fluid inclusions are being increasingly used in basin analysis and petroleum geology (Munz, 2001). The applications can be classified into: (1) the use of hydrocarbon fluid inclusions as direct records of hydrocarbon migration and charge history, (2) the reconstruction of the P-T history of a basin in relation to the development of hydrocarbon resources using paired aqueous and hydrocarbon inclusions, and (3) the use of bulk analyses of fluid-inclusion compositions as a tool in hydrocarbon exploration. Hydrocarbon fluid inclusions have been used as tracers of hydrocarbon migration events in Paleozoic basins in eastern Canada, and the regional scale variation of hydrocarbon inclusion types is related to tectonic setting and thermal conditions (Chi *et al.*, 2000). The frequency of quartz grains containing oil inclusions (GOI) in sandstone reservoirs has been used to study the charge history and evolution of oil-water contact (Lisk *et al.*, 2002). The PVTX studies of hydrocarbon fluid inclusions have been used to constrain the P-T history of an oil field (Aplin *et al.*, 2000). Bulk analysis of hydrocarbon fluid inclusions, or fluid inclusion stratigraphy (FIS), has been used in petroleum exploration related studies (Barclay *et al.*, 2000; Parnell, 2001).

Melt inclusions have been applied in the study of intrusive, extrusive, and mantle environments for a long time (Roedder, 1984). Such applications have increased rapidly in

recent years, as indicated by a simple search in "GeoRef" using "melt inclusions" as key words. The results of the search indicate 66 papers for the period from the year of 1975 to 1985, 198 papers from 1985 to 1995, and 345 papers from 1995 to 2002. As reviewed by Frezzotti (2001), most studies on melt inclusions in the last 20 years have been on high-temperature experiments (*i. e.*, microthermometry). In more recent studies, much attention has been paid to the use of chemical analysis of melt inclusions to characterize the chemical evolution of magmatic systems, the volatile contents of silicate-melt inclusions, and the behaviour of sulphur species (Frezzotti, 2001). Melt and fluid inclusions have been used as direct evidence of magmatic immiscibility (Roedder, 1992), including silicate-sulfide-carbonate immiscibility in the upper mantle (Andersen and Neumann, 2001). The application of melt inclusions in the study of earth interior processes has been one of the focuses of recent studies, as reflected in a special volume of Chemical Geology on melt inclusions (Volume 183, 2002).

Concluding remarks

In summary, there have been significant advances in the last two decades in fluid-inclusion research and its applications, especially in the development of the concept of 'fluid-inclusion assemblage', in the use of synthetic fluid inclusions and hydrothermal diamond-anvil cells in PVTX studies, in the development of Laser-Raman and LA-ICP-MS techniques, and in the increasing applications of fluid inclusions in various branches of earth science. The research in recent years has emphasized, and will continue to emphasize, the proper use of the FIA concept. The PVTX properties of aqueous-hydrocarbon systems will also be one of the focuses of research in the future. The Laser-Raman and LA-ICP-MS techniques will continue to be improved, and techniques enabling isotope analysis of single-generation fluid inclusions will be developed. Fluid inclusions will continue to be an important material for ore deposit research, and its usage will continue its expansion to other fields of earth science, especially in petroleum geology and the study of magmatic and earth interior processes.

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References

- Anderson A J, Clark A H, Ma X-P, Palmer G R, Macarthur J D, Bodnar R J and Roedder E. 1989. Proton-induced X-ray and gamma-ray emission analysis of unopened fluid inclusions. *Econ. Geol.*, 84: 924–939
- Anderson T and Neumann E-R. 2001. Fluid inclusions in mantle xenoliths. *Lithos*, 55: 301–320
- Angus S, Armstrong B and Reuck K M. 1976. International thermodynamic table of fluid state-3, carbon dioxide. Pergamon Press, 1–385
- Angus S, Armstrong B and Reuck K M. 1978. International thermodynamic table of fluid state-5, methane. Pergamon Press, 1–251
- Angus S, Armstrong B and Reuck K M. 1979. International thermodynamic table of fluid state-6, nitrogen. Pergamon Press, 1–385
- Aplin A C, Larter S R, Bigge M A, Macleod G, Swarbrick R E and Grunberger D. 2000. PVTX history of the North Sea's Judy oilfield. *J. Geochem. Explor.*, 69: 641–644
- Aplin A C, Macleod G, Larter S R, Pedersen K S, Sorensen H and Booth T. 1999. Combined use of confocal laser scanning microscopy and PVT simulation for estimating the composition and physical properties of petroleum in fluid inclusions. *Marine Petrol. Geol.*, 16: 97–110
- Bakker R J. 1999. Adaptation of the Bowers and Helgeson (1983) equation of state to the $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2-\text{NaCl}$ system. *Chem. Geol.*, 154: 225–236
- Bakker R J and Diamond L W. 2000. Determination of the composition and molar volume of $\text{H}_2\text{O}-\text{CO}_2$ fluid inclusions by microthermometry. *Geochim. Cosmochim. Acta*, 64: 1753–1764
- Bakker R J, Dubessy J and Cathelineau M. 1996. Improvements in clathrate modeling. I. The $\text{H}_2\text{O}-\text{CO}_2$ system with various salts. *Geochim. Cosmochim. Acta*, 60: 1657–1681
- Banks D A, Green R, Cliff R A and Yardley B W D. 2000. Chlorine isotopes in fluid inclusions: Determination of the origins of salinity in magmatic fluids. *Geochim. Cosmochim. Acta*, 64: 1785–1789
- Banks D A, Yardley B W D, Campbell A R and Jarvis K E. 1994. REE compositions of an aqueous magmatic fluid: A fluid inclusion study from Capitan Pluton, New Mexico, USA. *Chem. Geol.*, 113: 259–272
- Barclay S A, Worden R H, Parnell J, Hall D L and Sterner S M. 2000. Assessment of fluid contacts and compartmentalization in sandstone reservoirs using fluid inclusions: an example from the Magnus oil field, North Sea. *AAPG Bull.*, 84: 489–504
- Belkin H E, De Vivo B, Torok K and Webster J D. 1998. Pre-eruptive volatile content, melt-inclusion chemistry, and microthermometry of interplinian Vesuvius lavas (pre-AD1631). *J. Volcanol. Geoth. Res.*, 82: 79–95
- Bischoff J L. 1991. Densities of liquids and vapors in boiling $\text{NaCl}-\text{H}_2\text{O}$ solutions; a PVTX summary from 300° to 500°C. *Am. J. Sci.*, 291: 309–338
- Bischoff J L, Rosenbauer R J and Pitzer K S. 1986. The system $\text{NaCl}-\text{H}_2\text{O}$: relations of vapor-liquid near the critical temperature of water and of vapor-liquid-halite from 300° to 500°C. *Geochim. Cosmochim. Acta*, 50: 1437–1444
- Bischoff J L and Pitzer K S. 1989. Liquid-vapor relationships for the system $\text{NaCl}-\text{H}_2\text{O}$: Summary of the P-T-x surface from 300° to 500°C. *Am. J. Sci.*, 289: 217–248
- Bodnar R J. 1993. Revised equation and table for determining the freezing point depression of $\text{H}_2\text{O}-\text{NaCl}$ solutions. *Geochim. Cosmochim. Acta*, 57: 683–684
- Bodnar R J, Burnham C W and Sterner S M. 1985. Synthetic fluid inclusions in natural quartz. III. Determination of phase equilibrium properties in the system $\text{H}_2\text{O}-\text{NaCl}$ to 1000°C and 1500 bars. *Geochim. Cosmochim. Acta*, 49: 1861–1873
- Bodnar R J and Sterner S M. 1985. Synthetic fluid inclusions in natural quartz II. Application to PVT studies. *Geochim. Cosmochim. Acta*, 49: 1866–1859
- Bodnar R J, Sterner S M and Hall D L. 1988. Salty: a FORTRAN program to calculate compositions of fluid inclusions in the system $\text{NaCl}-\text{KCl}-\text{H}_2\text{O}$. *Computers and Geosciences*, 15: 19–41
- Boiron M C and Dubessy J. 1994. Determination of fluid inclusion compositions. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals"* (Pontignano-Siena, Sep. 1-4, 1994): 45–72
- Bottinga Y and Richet P. 1981. High pressure and temperature equation of state and calculation of the thermodynamic properties of gaseous carbon dioxide. *Am. J. Sci.*, 281: 615–660
- Boullier A-M and Robert F. 1992. Paleoseismic events recorded in Archean gold-quartz vein networks, Val d'Or, Abitibi, Quebec, Canada. *J. Struct. Geol.*, 14: 161–179
- Bower T S and Helgeson H C. 1983. Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ on phase relations in geologic systems: Equation of state for $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ at high pressures and temperatures. *Geochim. Cosmochim. Acta*, 47: 1247–1275
- Brodholt J P. 1998. Molecular dynamics simulations of aqueous NaCl solutions at high pressures and temperatures. *Chem. Geol.*, 151: 11–19
- Brown P E. 1989. FLINCOR: A microcomputer program for the reduction and investigation of fluid inclusion data. *Am. Mineral.*, 74: 1390–1393
- Brown P E. 1998. Fluid inclusion modeling for hydrothermal systems. In: Richards J P and Larson P B (eds.), *Techniques in hydrothermal ore deposits geology. Rev. Econ. Geol.*, 10: 151–171
- Brown P E and Hagemann S G. 1994. MacFlincor: A computer program for fluid inclusion data reduction and manipulation. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals"* (Pontignano-Siena, Sep. 1-4, 1994): 231–250
- Brown P E and Lamb W M. 1986. Mixing of $\text{H}_2\text{O}-\text{CO}_2$ in fluid inclusions: Geobarometry and Archean gold deposits. *Geochim. Cosmochim. Acta*, 50: 847–852
- Brown P E and Lamb W M. 1989. P-V-T properties of fluids in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$: New graphical presentations and implications for fluid inclusion studies. *Geochim. Cosmochim. Acta*, 53: 1209–1221
- Burke E A. 2001. Raman microspectrometry of fluid inclusions. *Lithos*, 55: 139–158
- Burruss R C. 1981. Analysis of phase equilibria in $\text{C}-\text{O}-\text{H}-\text{S}$ fluid inclusions. In: Hollister L S and Crawford M L (eds.), *Fluid*

- Inclusions: Applications to Petrology. Mineral. Assoc. Can., Short Course Handbook, 6: 39–74
- Campbell A R and Robinson-Cook S. 1987. Infrared fluid inclusion microthermometry on coexisting wolframite and quartz. *Econ. Geol.*, 82: 1640–1645
- Chi G, Bertrand R and Lavoie D. 2000. Regional-scale variation of characteristics of hydrocarbon fluid inclusions and thermal conditions along the Paleozoic Laurentian continental margin in eastern Quebec, Canada. *Bull. Can. Petrol. Geol.*, 48: 193–211
- Chou I-M. 1987. Phase relations in the system NaCl-KCl-H₂O. III. Solubilities of halite in vapor-saturated liquids above 445°C and redetermination of phase equilibrium properties in the system NaCl-H₂O to 1000°C and 1500 bars. *Geochim. Cosmochim. Acta*, 51: 1965–1975
- Chou I-M, Blank J G, Goncharov A F, Mao H K and Hemley R J. 1998. In situ observations of a high-pressure phase of H₂O ice. *Science*, 281: 809–812
- Chou I-M, Sharma A, Burruss R C, Hemley R J, Goncharov A F, Stern L A and Kirby S H. 2001. Diamond-anvil cell observations of a new methane hydrate phase in the 100-MPa pressure range. *J. Phys. Chem., A* 105: 4664–4668
- Chou I-M, Shen A H and Esset W A. 1994. Applications of the hydrothermal diamond-anvil cell in fluid-inclusion research. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals" (Pontignano-Siena, Sep. 1-4, 1994): 215–230
- Christensen J N, Halliday A N, Leigh K E, Randell R N and Kesler S E. 1995. Direct dating of sulfides by Rb-Sr: A critical test using the Polariss Mississippi Valley-type Zn-Pb deposit. *Geochim. Cosmochim. Acta*, 59: 5191–5197
- Crawford M L. 1981. Phase equilibrium in aqueous fluid inclusions. In: Hollister L S and Crawford M L (eds.), *Fluid Inclusions: Applications to Petrology*. Mineral. Assoc. Can., Short Course Handbook, 6: 75–100
- Darling R S. 1991. An extended equation to calculate NaCl contents from final clathrate melting temperatures in H₂O-CO₂-NaCl fluid inclusions: Implications for P-T isochore location. *Geochim. Cosmochim. Acta*, 55: 3869–3871
- Deloule E, Paillat O, Pichavant M and Scaillet B. 1995. Ion microprobe determination of water in silicate glasses: methods and applications. *Chem. Geol.*, 125: 19–28
- Der Channer D M, Bray C J and Spooner E T C. 1999. Integrated cation-anion volatile fluid inclusion analysis by gas and ion chromatography: methodology and examples. *Chem. Geol.*, 154: 59–82
- De Vivo B and Frezzotti M L (eds.). 1994. *Fluid inclusions in minerals: Methods and applications*. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals" (Pontignano-Siena, Sep. 1-4, 1994): 1–376
- Diamond L W. 1992. Stability of CO₂ clathrate hydrate + CO₂ liquid + CO₂ vapor + aqueous KCl-NaCl solutions; Experimental determination and application to salinity estimates of fluid inclusions. *Geochim. Cosmochim. Acta*, 56: 273–280
- Diamond L W. 1994. Salinity of multivolatile fluid inclusions determined from clathrate hydrate stability. *Geochim. Cosmochim. Acta*, 58: 19–41.
- Diamond L W. 2001. Review of the systematics of CO₂-H₂O fluid inclusions. *Lithos*, 55: 69–99
- Duan Z H, Moller N and Weare J H. 1992a. An equation of state for the CH₄-CO₂-H₂O system; I. Pure systems from 0 to 1000°C and 0 to 1000 bar. *Geochim. Cosmochim. Acta*, 56: 2605–2617
- Duan Z H, Moller N and Weare J H. 1992b. An equation of state for the CH₄-CO₂-H₂O system; II. Mixtures from 50 to 1000°C and 0 to 1000 bar. *Geochim. Cosmochim. Acta*, 56: 2619–2631
- Duan Z, Moller N, Greenberg J and Weare J H. 1992c. The prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar. *Geochim. Cosmochim. Acta*, 56: 1451–1460
- Duan Z, Moller N and Weare J H. 1995. Equation of state for the NaCl-H₂O-CO₂ system; prediction of phase equilibria and volumetric properties. *Geochim. Cosmochim. Acta*, 59: 2869–2882
- Duan Z H, Moller N and Weare J H. 2000. Accurate prediction of the thermodynamic properties of fluids in the system H₂O-CO₂-CH₄-N₂ up to 2000 K and 100 kbar from a corresponding states/one fluid equation of state. *Geochim. Cosmochim. Acta*, 64: 1069–1075
- Dubessy J. 1994. Single component systems; phase diagrams and their application to fluid inclusions. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals" (Pontignano-Siena, Sep. 1-4, 1994): 95–115
- Dubessy J, Buschaert S, Lamb W, Pironon J and Thierry R. 2001. Methane-bearing aqueous fluid inclusions; raman analysis, thermodynamic modeling and application to petroleum basins. *Chem. Geol.*, 173: 193–205
- Dubessy J and Thierry R. 1994. Equations of state for modeling phase transitions in the system CO₂-CH₄-N₂; applied to microthermometry of fluid inclusions. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals" (Pontignano-Siena, Sep. 1-4, 1994): 159–190
- Dubessy J, Thierry R and Canals M. 1992. Modeling of phase equilibrium involving mixed gas clathrates; application to the determination of molar volume of the vapor phase and salinity of the aqueous solution in fluid inclusions. *Eur. J. Mineral.*, 4: 873–884
- Dubois M and Marignac C. 1997. The H₂O-NaCl-MgCl₂ ternary phase diagram with special application to fluid inclusion studies. *Econ. Geol.*, 92: 114–119
- Fabre C, Boiron M C, Dubessy J and Moissette A. 1999. Determination of ions in individual fluid inclusions by laser ablation optical emission spectroscopy: development and applications to natural fluid inclusions. *J. Anal. Atom. Spectr.*, 14: 913–922
- Frantz J D, Popp R K and Hoering T C. 1992. The compositional limits of fluid immiscibility in the system H₂O-NaCl-CO₂ as determined with the use of synthetic fluid inclusions in conjunction with mass spectrometry. *Chem. Geol.*, 98: 237–255
- Frezzotti M-L. 2001. Silicate-melt inclusions in magmatic rocks; applications to petrology. *Lithos*, 55: 273–299
- George S C, Krieger F W, Eadington P J, Quezada R A, Greenwood P F, Eisenberg L I, Hamilton P J and Wilson M A. 1997. Geochemical comparison of oil-bearing fluid inclusions and produced oil from the Toro Sandstone, Papua New Guinea. *Org. Geochem.*, 26: 155–173

- Gibbard H F and Fong S L. 1975. Freezing points and related properties of electrolyte solutions. III. The systems $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ and $\text{NaCl}-\text{BaCl}_2-\text{H}_2\text{O}$. *J. Solu. Chem.*, 4: 863–872
- Gibbard H F and Gossmann A. 1974. Freezing points of electrolyte solutions. I. Mixtures of sodium chloride and magnesium chloride in water. *J. Solu. Chem.*, 3: 385–394
- Gibert F, Guillaume D and Laporte D. 1998. Importance of fluid immiscibility in the $\text{H}_2\text{O}-\text{NaCl}-\text{CO}_2$ system and selective CO_2 entrapment in granulites: Experimental phase diagram at 5–7 kbar, 900 °C and wetting textures. *Euro. J. Mineral.*, 10: 1109–1123
- Goldstein R H. 2001. Fluid inclusions in sedimentary and diagenetic systems. *Lithos*, 55: 159–193
- Goldstein R H and Reynolds T J. 1994. Systematics of fluid inclusions in diagenetic minerals. *SEPM Short Course*, 31: 1–199
- Grevel K D. 1990. A modified Redlich-Kwong equation of state for methane at temperatures between 150 K and 1500 K and pressures up to 300 kbar. In *thermodynamic Data Systematics Symposium*. Uppsala University, Sweden
- Gunther D, Audetat A, Frischknecht R and Heinrich C A. 1998. Quantitative analysis of major, minor and trace elements in fluid inclusions using laser ablation inductively coupled plasma mass spectrometry. *J. Anal. Atom. Spectr.*, 13: 263–270
- Haar L, Gallagher J S and Kell S J. 1984. NBS/NRC steam tables. Thermodynamic and transport properties and computer programs for vapour and liquid states of water in SI units. New York: McGraw-Hill, 1–318
- Halbach H and Chatterjee N D. 1982. An empirical Redlich-Kwong-type equation of state for water to 1000 °C and 200 kbar. *Contrib. Mineral. Petrol.*, 79: 337–345
- Hall D L, Sterner S M and Bodnar R J. 1988. Freezing point depression of $\text{NaCl}-\text{KCl}-\text{H}_2\text{O}$ solutions. *Econ. Geol.*, 83: 197–202
- Haynes F M. 1985. Detection of fluid compositions by sequential freezing. *Econ. Geol.*, 80: 1436–1439
- Haynes F M, Sterner S M and Bodnar R J. 1988. Synthetic fluid inclusions in natural quartz. IV. Chemical analyses of fluid inclusions by SEM/EDA; Evaluation of method. *Geochim. Cosmochim. Acta*, 52: 969–977
- Hazen R H and Roedder E. 2001. How old are bacteria from the Permian age? *Nature*, 411: 155
- Heinrich C A, Gunther D, Audetat A, Ulrich T and Frischknecht R. 1999. Metal fractionation between magmatic brine and vapour, determined by microanalysis of fluid inclusions. *Geol.*, 27: 755–758
- Herskowitz M and Kisch H J. 1984. An algorithm for finding composition, molar volume and isochores of CO_2-CH_4 fluid inclusions from T_h and T_{fm} (for $T_h < T_{fm}$). *Geochim. Cosmochim. Acta*, 48: 1581–1587
- Heyen G, Ramboz C and Dubessy J. 1982. Modeling of phase equilibria in the CO_2-CH_4 below 50 °C and 100 bar: Application to inclusion fluids. *Compte Rendu Acad. Sciences Paris*, 294, ser. II: 203–206
- Hill P G. 1990. A unified fundamental equation for the thermodynamic properties of H_2O . *J. Phys. Chem. Ref. Data*, 19: 1233–1274
- Holloway J R. 1981. Compositions and volumes of supercritical fluids in the earth's crust. In: Hollister L S and Crawford M L (eds). *Fluid Inclusions: Applications to Petrology*. Mineral. Assoc. Can., Short Course Handbook, 6: 13–38
- Huizenga J-M. 2001. Thermodynamic modelling of C-O-H fluids. *Lithos*, 55: 101–114
- Jacobs G K and Kerrick D M. 1981. Methane: an equation of state with application to the ternary system $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4$. *Geochim. Cosmochim. Acta*, 45: 607–614
- Jacobsen R T, Stewart R B and Jahangiri M. 1986. Thermodynamic properties of nitrogen from freezing line to 2000 K at pressure to 1000 MPa. *J. Phys. Chem. Ref. Data*, 15: 735–909
- Kerkhof A M van den. 1990. Isochoric phase diagrams in the systems CO_2-CH_4 and CO_2-N_2 : Application to fluid inclusions. *Geochim. Cosmochim. Acta*, 54: 621–629
- Kerkhof A M van den and Hein U F. 1992. H_2S -bearing systems. *PACROFI-IV Programs & Abstracts*, 164–172
- Kerkhof A M van den and Hein U F. 2001. Fluid inclusion petrography. *Lithos*, 55: 27–471
- Kerkhof A M van den and Thiery K. 1994. Phase transitions and density calculation in the $\text{CO}_2-\text{CH}_4-\text{N}_2$ system. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals" (Pontignano-Siena, Sep. 1-4, 1994): 171–190
- Kerkhof A M van den and Thiery R. 2001. Carbonic inclusions. *Lithos*, 55: 49–68
- Kerrick D M and Jacobs G K. 1981. A modified Redlich-Kwong equation of state for H_2O , CO_2 , and $\text{H}_2\text{O}-\text{CO}_2$ mixtures at elevated pressures and temperatures. *Am. J. Sci.*, 281: 735–767
- Kesler S E, Vennemann T W, Frederickson C, Breithaupt A, Vazquez R and Furman F C. 1997. Hydrogen and oxygen isotope evidence for origin of MVT-forming brines, southern Appalachians. *Geochim. Cosmochim. Acta*, 61: 1513–1523
- Knight C L and Bodnar R J. 1989. Synthetic fluid inclusions. IX. Critical PVTX properties of $\text{NaCl}-\text{H}_2\text{O}$ solutions. *Geochim. Cosmochim. Acta*, 53: 3–8
- Kovalevich V M, Peryt T M and Petrichenko O I. 1998. Secular variation in seawater chemistry during the Phanerozoic as indicated by brine inclusions in halite. *J. Geol.*, 106: 695–712
- Lamb W M, Popp R K and Boockoff L A. 1996. The determination of phase relations in the $\text{CH}_4-\text{H}_2\text{O}-\text{NaCl}$ system at 1 kbar, 400° to 600 °C using synthetic fluid inclusions. *Geochim. Cosmochim. Acta*, 60: 1885–1897
- Li Z. 1994. The silicate melt inclusions in igneous rocks. In: De Vivo B and Frezzotti M L (eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Short Course of the Working Group (IMA) "Fluid Inclusions in Minerals" (Pontignano-Siena, Sep. 1-4, 1994): 73–94
- Lisk M, O'Brien G W and Eadington P J. 2002. Quantitative evaluation of the oil-leg potential in the Oliver gas field, Timor Sea, Australia. *AAPG Bull.*, 86: 1531–1542
- Lu H and Guo D. 2000. Progress and trends of researches on fluid inclusions. *Geol. Rev.*, 46: 385–392
- Luders V and Ziemann M. 1999. Possibilities and limits of infrared light microthermometry applied to studies of pyrite-hosted fluid inclusions. *Chem. Geol.*, 154: 169–178
- Mader U K and Berman R G. 1991. An equation of state for carbon dioxide to high pressure and temperature. *Am. Mineral.*, 76: 1547–1559
- Menez B, Philippot P, Bonnin-Mosbah M, Simionovici A and Gibert F. 2002. Analysis of individual fluid inclusions using Synchrotron X-ray Fluorescence microprobe: progress toward calibration for trace elements. *Geochim. Cosmochim. Acta*, 66:

- 561–576
- Moore J N, Norman D I and Kennedy B M. 2001. Fluid inclusion gas composition from an active magmatic-hydrothermal system; a case study of the Geysers geothermal field, USA. *Chem. Geol.*, 173, 3–30
- Munz I A. 2001. Petroleum inclusions in sedimentary basins; systematics, analytical methods and applications. *Lithos*, 55, 195–212
- Murphy P J and Roberts S. 1997. Melting and nucleation behavior of clathrates in multivolatile fluid inclusions; evidence of thermodynamic disequilibrium. *Chem. Geol.*, 135, 1–20
- Nakai S, Halliday A N, Kesler S E and Jones H D. 1990. Rb-Sr dating of sphalerites from Tennessee and the genesis of Mississippi Valley type ore deposits. *Nature*, 346, 354–357
- Oakes C S, Bodnar R J and Simonson J M. 1990a. The system NaCl-CaCl₂-H₂O. I. The ice liquidus at 1 atm total pressure. *Geochim. Cosmochim. Acta*, 54, 603–610
- Oakes S C, Bodnar R J, Simonson H M and Pitzer K S. 1994. Critical and supercritical properties for 0.3 to 3.0 mol. Kg⁻¹ CaCl₂ (aq). *Geochim. Cosmochim. Acta*, 58, 2421–2431
- Oakes C S, Simonson J M and Bodnar R J. 1990b. The system NaCl-CaCl₂-H₂O. 2. Densities for ionic strengths of 0.1–19.2 mol. kg⁻¹ at 298.15 and 306.15 K and at 0.1 MPa. *J. Chem. Eng. Data*, 35, 304–309
- Parnell J, Middleton D, Chen H H and Hall D. 2001. The use of integrated fluid inclusion studies in constraining oil charge history and reservoir compartmentation; examples from the Jeanne d'Arc Basin, offshore Newfoundland. *Mar. Petrol. Geol.*, 18, 535–549
- Pethke T and Diamond L. 1995. Rb-Sr isotopic analysis of fluid inclusions in quartz; evaluation of bulk extraction procedures and geochronometer systematics using synthetic fluid inclusions. *Geochim. Cosmochim. Acta*, 59, 4009–4027
- Pironon J, Thierry R, Ayt Ougougdal M, Teinturier S, Beaudoin G and Walgenwitz G. 2001. FT-IR measurements of petroleum fluid inclusions; methane, n-alkanes and carbon dioxide quantitative analysis. *Geofluids*, 1, 2–10
- Prausnitz J M, Lichtenthaler R N and Gomes de Azevedo E. 1986. *Molecular thermodynamics of fluid-phase equilibria*; Prentice-Hall, 1–600
- Ramsey M H, Coles B J, Rankin A H and Wilkinson J J. 1992. Single fluid inclusion analysis by laser ablation-inductively coupled plasma-atomic emission spectrometry; quantification and validation. *J. Anal. Atom. Spectr.*, 7, 587–593
- Roedder E. 1984. Fluid inclusions. *Reviews in Mineralogy*, 12, 1–644
- Roedder E. 1990. Fluid inclusion analysis — prologue and epilogue. *Geochim. Cosmochim. Acta*, 54, 495–507
- Roedder E. 1992. Fluid inclusion evidence for immiscibility in magmatic differentiation. *Geochim. Cosmochim. Acta*, 56, 5–20
- Roedder E and Bodnar R J. 1997. Fluid inclusion studies of hydrothermal ore deposits. In: Barnes H L (ed), *Geochemistry of hydrothermal ore deposits*. John Wiley & Sons Inc; 657–698.
- Ryan C G, Heinrich C A and Mernagh T P. 1993. PIXE microanalysis of fluid inclusions and its application to study ore metal segregation between magmatic brine and vapour. *Nucl. Instrum. Methods Phys. Res.*, B77, 463–471
- Salvi S and Williams-Jones A E. 1997. Fluid-inclusion volatile analysis by gas chromatography; application of a wide-bore porous-polymer capillary column to the separation of organic and inorganic compounds. *Can. Mineral.*, 35, 1391–1414
- Saul A and Wagner W. 1989. A fundamental equation for water covering the range from the melting line to 1273 K at pressures up to 25000 MPa. *J. Phys. Chem. Ref. Data*, 18, 370–375
- Saxena S K and Fei Y. 1987. Fluids at crustal pressures and temperatures I. Pure species. *Contrib. Mineral. Petrol.*, 95, 370–375
- Scambelluri M and Philippot P. 2001. Deep fluids in subduction zones. *Lithos*, 55, 213–227
- Schmidt C, Bodnar R J. 2000. Synthetic fluid inclusions; XVI. PVTX properties in the system H₂O-NaCl-CO₂ at elevated temperatures, pressures, and salinities. *Geochim. Cosmochim. Acta*, 64, 3853–3869
- Schmidt C, Rizzo K M and Bodnar R J. 1995. Synthetic fluid inclusions; XIII. Experimental determination of PVT properties in the system H₂O + 40 wt% NaCl + 5 mol% CO₂ at elevated temperature and pressure. *Geochim. Cosmochim. Acta*, 59, 3953–3959
- Shepherd T J and Rankin A H. 1998. Fluid inclusion techniques of analysis. In: Richards J P and Larson P B (eds). *Techniques in hydrothermal ore deposits geology*. *Rev. Econ. Geol.*, 10, 125–149
- Shmulovich K I and Graham C M. 1999. An experimental study of phase equilibria in the system H₂O-CO₂-NaCl at 800°C and 9 kbar. *Contrib. Mineral. Petrol.*, 136, 247–257
- Shmulovich K I and Shmonov V M. 1975. Fugacity coefficients for CO₂ from 1.0232 to 10000 bar and 450–1300K. *Geochemistry International*, 12, 202–206
- Simon K. 2001. Does delta D from fluid inclusion in quartz reflect the original hydrothermal fluid? *Chem. Geol.*, 177, 483–495.
- Spenser R J, Moller N and Weare J H. 1990. The prediction of mineral solubilities in natural waters. A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures below 25°C. *Geochim. Cosmochim. Acta*, 54, 575–590
- Stasiuk L D and Snowdon L R. 1997. Fluorescence microspectrometry of synthetic and natural hydrocarbon fluid inclusions; crude oil chemistry, density and application to petroleum migration. *Appl. Geochem.*, 12, 229–241
- Sterner S M and Bodnar R J. 1984. Synthetic fluid inclusions in natural quartz I. Compositional types synthesized and applications to experimental geochemistry. *Geochim. Cosmochim. Acta*, 48, 2659–2668
- Sterner S M and Bodnar R J. 1991. Synthetic fluid inclusions; X. Experimental determination of P-V-T-X properties in the CO₂-H₂O system to 6 Kb and 700°C. *Am. J. Sci.*, 291, 1–54
- Sterner S M, Hall D L and Bodnar R J. 1988. Synthetic fluid inclusions. V. Solubility relations in the system NaCl-KCl-H₂O under vapor-saturated conditions. *Geochim. Cosmochim. Acta*, 52, 989–1005
- Sterner S M and Pitzer K S. 1994. An equation of state for carbon dioxide valid from zero to extreme pressures. *Contrib. Mineral. Petrol.*, 117, 362–374
- Swanenberg H E C. 1979. Phase equilibria in carbonic systems, and their application to freezing studies of fluid inclusions. *Contrib. Mineral. Petrol.*, 68, 303–306
- Teinturier S, Pironon J and Walgenwitz F. 2002. Validation of the PVT modeling of petroleum using synthetic fluid inclusions. *PACROFI VIII, Program with Abstract* (Halifax, Jul. 22–24, 2002); 100–102
- Thierry R, Kerkhof A M van den and Dubessy J. 1994. vX properties

- modeling of CH_4 - CO_2 and CO_2 - N_2 fluid inclusions ($T < 31^\circ\text{C}$, $P < 400$ bar). *Eur. J. Mineral.*, 6: 753–771
- Thiery R, Pironon J, Walgenwitz F and Montel F. 2000. PIT (Petroleum Inclusion Thermodynamic); a new modeling tool for the characterization of hydrocarbon fluid inclusions from volumetric and microthermometric measurements. *J. Geochem. Explor.*, 69–70: 701–704
- Timofeeff M N, Lowenstein T K and Blackburn W H. 2000. ESEM-EDS; an improved technique for major element chemical analysis of fluid inclusions. *Chem. Geol.*, 164: 171–182
- Touret J and Bottinga Y 1979. Equation d'état pour le CO_2 ; application aux inclusions carboniques. *Bull. Mineral.*, 102: 577–583
- Touret J and Guilhaumou N. 1984. Characterization of H_2S -bearing fluid inclusions. *Bull. Mineral.*, 107: 181–188
- Vanko D A, Bodnar R J and Sterner S M. 1988. Synthetic fluid inclusions. VIII. Vapor-saturated halite solubility in part of the system $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$, with application to fluid inclusions from oceanic hydrothermal systems. *Geochim. Cosmochim. Acta*, 52: 2451–2456
- Vargaftik N B. 1975. Tables on the thermophysical properties of liquids and gases in normal and dissociated states; John Wiley and Sons, 1–755
- Villa I M. 2001. Radiogenic isotopes in fluid inclusions. *Lithos*, 55: 115–124
- Viti C and Frezzotti M-L. 2001. Transmission electron microscopy applied to fluid inclusion investigations. *Lithos*, 55: 125–138
- Vreeland R H, Rosenzweig W D and Powers D W. 2000. Isolation of a 250 million year old halotolerant bacterium from a primary salt crystal. *Nature*, 407: 897–900
- Wilkinson J J. 1990. The role of metamorphic fluids in the development of the Cornubian orofield; Fluid inclusion evidence from south Cornwall. *Mineral. Magazine*, 54: 219–230
- Wilkinson J J. 2001. Fluid inclusions in hydrothermal ore deposits. *Lithos*, 55: 229–272
- Williams-Jones A E and Samson I M. 1990. Theoretical estimation of halite solubility in the system $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$; Applications to fluid inclusions. *Can. Mineral.*, 28: 299–304
- Withers A C, Kohn S C, Brooker R A and Wood B J. 2000. A new method for determining the P-V-T properties of high-density H_2O using NMR; Results at 1.4–4.0 GPa and 700–1100 $^\circ\text{C}$. *Geochim. Cosmochim. Acta*, 64: 1051–1057
- Wolf A V, Brown M G and Prentiss P G. 1986. Concentrative properties of aqueous solutions; conversion tables. *Handbook of Chemistry and Physics*, 67th ed; Cleveland, CRC Press
- Yang K and Scott S D. 1996. Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. *Nature*, 383: 420–423
- Zhang Y-G. 1997. Molar volumes of the binary system $\text{H}_2\text{O-CH}_4$ at high temperatures and pressures. *Scientia Geologica Sinica*, 32: 295–307
- Zhang Y-G and Frantz J D. 1987. Determination of the homogenization temperatures and densities of supercritical fluids in the system $\text{NaCl-KCl-CaCl}_2\text{-H}_2\text{O}$ using synthetic fluid inclusions. *Chem. Geol.*, 64: 335–350
- Zhang Y-G and Frantz J D. 1989. Experimental determination of the compositional limits of immiscibility in the system $\text{CaCl}_2\text{-H}_2\text{O-CO}_2$ at high temperatures and pressures using synthetic fluid inclusions. *Chem. Geol.*, 74: 289–308
- Zhang Y-G and Frantz J D. 1992. Hydrothermal reactions involving equilibrium between minerals and mixed volatiles; 2. Investigation of fluid properties in the $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O}$ system using synthetic fluid inclusions. *Chem. Geol.*, 100: 51–72