THE EFFECT OF HYDROGEN BONDING ON THE STRUCTURE AND PROPERTIES OF AQUEOUS HYDROTHERMAL FLUIDS: COMPUTER SIMULATION STUDIES. A. G. Kalinichev1,2, 1Department of Geology, University of Illinois, Urbana IL 61801, USA (andreyk@hercules.geology.uiuc.edu), 2Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia.

**Introduction:** Accurate thermodynamic modeling of hydrothermal fluids is complicated by the presence of specific hydrogen bonding interactions between water molecules. The question of the ranges of temperature and pressure (density) where these specific interactions can significantly influence the observable properties of water is very important for the construction of realistic thermodynamic and structural models of hydrothermal fluids. Several experimental sources suggest that some degree of H-bonding persists well into the supercritical region of water [1]. However, such evidences are often indirect and inconclusive. On the other hand, numerous Monte Carlo (MC) and molecular dynamics (MD) computer simulation studies of supercritical water have been performed over the last decade [2]. The advantage of computer “experiments” is in their ability to generate and analyze in detail spatial and energetic environments of every individual molecule or multi-molecular configuration, thus providing extremely useful micro-thermodynamic and micro-structural information on the molecular level, not available from any real physical measurement.

**Computer Simulations:** MC and MD simulations of water using several realistic intermolecular potential functions were carried out at more than 50 states covering a very wide range of thermodynamic conditions typical for many hydrothermal and metamorphic processes: $273 \leq T \leq 1273$ K; $0.02 \leq \rho \leq 1.67$ g/cm$^3$; $0.1 \leq P \leq 10,000$ MPa [2,3]. Simulated PVT-properties, as well as enthalpy, internal energy, heat capacity, isothermal compressibility, thermal expansion and self-diffusion coefficients agree surprisingly well with available experimental data, if one correctly accounts for some differences in the critical parameters between the models and real water. The simulated structure of supercritical water also agrees well with x-ray and neutron diffraction data, and is consistent with several other computer simulations using inherently different intermolecular potentials. This qualitatively and quantitatively correct behavior of many simulated properties over very wide ranges of thermodynamic conditions allows us to analyze with reasonable confidence the detailed temperature- and density dependencies of local spatial and energetic arrangements of water molecules leading to hydrogen bonding.

**Hydrogen Bonding under Hydrothermal Conditions:** Quantitative analysis of H-bonding in supercritical water was performed on the basis of hybrid distance-energy criterion of hydrogen bond formation [4]. With increasing temperature, the average number of H-bonds per a water molecule, $\langle n_{HB} \rangle$, decreases with the same slope for both liquid-like (≤1.0 g/cm$^3$) as well as vapor-like (≤0.2 g/cm$^3$) supercritical water. This result agrees well with all available estimates based on experimental data from various sources. Over the whole supercritical region, except for the most high-density states, $\langle n_{HB} \rangle$ is always below the percolation threshold (~1.6) indicating that the continuous percolating network of hydrogen bonds is broken. Nevertheless, up to 40% of H-bonds present in liquid water at room temperature can still be preserved under supercritical conditions. For a typical hydrothermal thermodynamic state ($T=673$ K; $P=80$ MPa; $\rho=0.66$ g/cm$^3$), average hydrogen bonds are almost 10% weaker energetically, 5% longer, and ~8° more bent, compared to those in normal liquid water.

**Clusterization in Supercritical Water:** Although the infinite percolating network of H-bonds largely breaks apart under hydrothermal conditions, individual water molecules for significant amount of time still remain bonded together in smaller molecular aggregates, or clusters [2]. Quantitative understanding of the size and structure of such clusters is important for many fundamental and practical reasons. For example, large pressure effects on the isotope fractionation between hydrothermal solutions and minerals can be explained by taking into account the degree of clusterization in water vapor [5].

Present simulation results demonstrate that even low-density hydrothermal fluid ($\rho<0.2$ g/cm$^3$) can contain relatively large H-bonded clusters, consisting of up to 10 water molecules. We observed no significant density dependence of relative abundances for topologically different water clusters, and chain-like clusters are found predominant. In contrast to the results of quantum chemical calculations for isolated water clusters, which identify ring-like clusters as the most stable energetically, such clusters are only rarely formed under hydrothermal conditions [6]. The fraction of pentamers topologically organized as complete tetrahedra is also insignificant under these conditions.