

Incorporation of Al, Mg, and water in opal-A: Evidence from speleothems

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ABSTRACT

Opal-A speleothems from a variety of caves show a wide range of composition, containing up to 5% Al_2O_3 and MgO. The infrared spectra of the samples show that the Al is substituting for Si, with OH groups compensating for the resultant charge imbalance. The Mg occurs as interstitial ions to which OH groups are bonded to balance the charge. Thus the hydroxyls in opal are present not only as surface silanol groups, but also as OH groups within the opal structure to balance the charge of the substituted Al and as OH groups bonded to interstitial elements like Mg.

INTRODUCTION

Opal is a naturally occurring hydrous “amorphous” silica mineral that forms in a variety of surface and near-surface environments (Fronzel, 1962; Wilding et al., 1977). Opal from many of these environments has been studied intensively, but little attention has been paid to occurrences of opal in caves as secondary mineral deposits (speleothems). In this study, the term “speleothem” is used in a general sense to encompass opals precipitated in caves from both high- and low-temperature solutions, i.e., to cover both hyalites and gel opals as defined by Langer and Flörke (1974).

Opal speleothems have been frequently recorded (Hill and Forti, 1986), but little detailed work has been carried out on them. However, the analytical data available show a wider range of composition than otherwise known for opal (Cody, 1980; Webb and Finlayson, 1984), so opal speleothems appear to have considerable potential for throwing new light on the way in which various minor elements are incorporated into the opal structure. Wilding et al. (1977) noted that impurities in opal may be occluded, chemisorbed, or in solid solution, but to date little work has been done on the relative contributions of these three processes to the minor-element composition of opal.

OCCURRENCES OF OPAL SPELEOTHEMS

Opal speleothems have been frequently recorded in lava caves and are also occasionally present in limestone caves, granite caves, and sandstone overhangs (Finlayson and Webb, 1985). Small irregular coralloids or botryoidal coatings are the most common form taken by the speleothems, although they also occur as stalactites, stalagmites, and flowstone (Hill and Forti, 1986). Maximum dimensions rarely exceed 5 cm.

For the present study, opal speleothems were obtained from two basalt caves in western Victoria, a basalt cave in southeast Queensland, and two granite caves in southeast Queensland. Several speleothems from a small area of each cave were combined to give a single sample, and in two caves, samples were collected at two different localities within the cave.

In addition speleothems were collected from a granite cave in southern California, U.S.A.; these samples contain interlayers of poorly crystallized sepiolite (a hydrous magnesium silicate clay mineral), which is useful for comparison with the opal speleothems.

Basalt caves

Much of western Victoria is occupied by a large volcanic province, containing basalts collectively known as the Newer Volcanics (Joyce, 1975). The main period of volcanicity probably commenced in the late Pliocene and continued into the Holocene (McDougall et al., 1966), so physiographic features, such as lava caves, are well preserved. More than 50 lava caves have been recorded in the Newer Volcanics (J. A. Webb, E. B. Joyce, and N. C. Stevens, unpub. manuscript) and two of these are known to contain opal speleothems: Skipton Cave and Mt. Hamilton Cave.

The exact age of the lavas surrounding these two caves is unknown, but in each case it is likely to be 2.5 Ma or less (Webb, 1985; J. A. Webb, E. B. Joyce, and N. C. Stevens, unpub. manuscript). Parts of the walls and ceilings of the two caves are covered with small opaline coralloids and stalactites. On one wall of the southernmost chamber in Mt. Hamilton Cave are abundant rosettes of acicular crystals; these are composed of opal and apparently represent pseudomorphs after a fibrous zeolite (Webb, 1985).

The Great Dividing Range in southeast Queensland is made up of 900 m of nearly horizontal basalts and minor trachytes of late Oligocene to early Miocene age (Webb et al., 1967). A small cave (Holy Jump Lava Cave) is present in basalt toward the top of the sequence. The walls of the cave are encrusted by secondary

silica minerals: glass-clear botryoidal layers of hyalite (opal-A) and milky stalactites and flowstone of opal-CT and chalcedony (Webb, 1979). Only the opal-A crusts were examined during the course of the present study.

Granite caves

The "Granite Belt" in southeast Queensland is a large area of granite terrane that contains a number of caves and sinking streams (Finlayson, 1982). Most of the caves have formed where a stream has developed an underground passage along a joint, and two (South Bald Rock Cave and River Cave) have opaline coralloids coating the undersides of boulders roofing the caves (Webb and Finlayson, 1984). South Bald Rock Cave also contains allophane flowstone on the walls and floor.

Extensive areas of granite terrane occur in California, and in one of these, about 100 km north-northeast of San Diego, is Cahuilla Creek Cave (Finlayson, 1985). This cave consists of granite boulders roofing a stream. Coralloids occur on the walls of the cave and flowstone on the floor; both speleothem types consist largely of banded calcite, although one of the coralloid samples contains very thin interlayers of poorly crystallized sepiolite.

MICROSTRUCTURE

Freshly broken surfaces of all the opaline speleothems were examined under the scanning-electron microscope. A variety of microstructures are evident, including glassy conchoidal fracture surfaces (Fig. 1c), irregular colloidal aggregates (Fig. 1a), and in one instance colloform or botryoidal surfaces (Fig. 1b). Similar microstructures have been documented previously for opal-A (e.g., Segnit et al., 1970, 1973).

ANALYTICAL METHODS AND RESULTS

Chemical analyses of the speleothems were carried out using X-ray fluorescence and an electron microprobe, and showed that several different minor elements are present (Table 1). Apart from Al and Mg, which will be discussed further below, these elements are present in very small amounts comparable to, or less than, those recorded in opal from other environments (Fron del, 1962; Wilding et al., 1977; Segnit and Jones, pers. comm.).

The X-ray diffraction patterns of all the opal speleothems are typical of opal-A (Jones and Segnit, 1971). Langer and Flörke (1974, p. 18) subdivided opal-A into two varieties: opal-AN (hyalite), with "no remarkable low angle X-ray scattering," and opal-AG, distinguished by "low angle scattering typical for gel-like structures of monocrystalline SiO_2 ." The speleothem samples all have XRD patterns very similar to the latter type, including the hyalite specimen from Holy Jump Lava Cave.

The infrared (IR) absorption spectra of the opal speleothems (Fig. 2) were obtained using pressed KBr discs (prepared in the standard manner, e.g., Russell, 1974) and a Jasco A302 spectrometer. Each disc contained 0.2 mg of sample and 200 mg of KBr, both accurately weighed. The samples were dry ground; grinding in alcohol is preferable for crystalline materials (Tuddenham and Lyon, 1960), but may lead to water loss in amorphous samples (C. Barraclough, pers. comm.). The lack

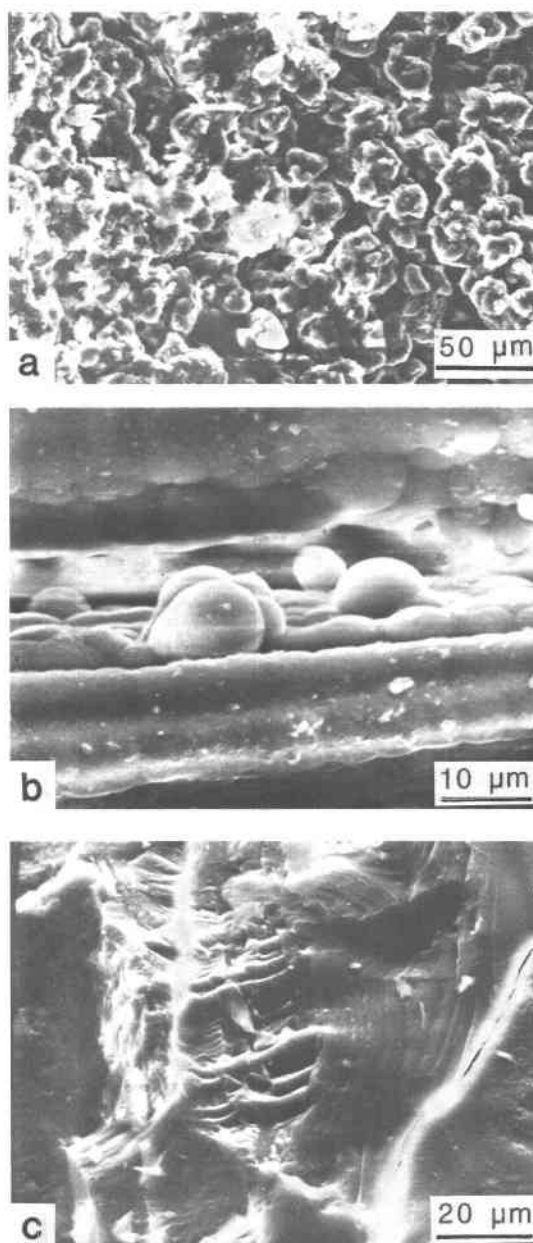


Fig. 1. Surface microstructures of opal speleothems under the SEM. (a) Colloidal aggregate (8416-12); coralloid from South Bald Rock Cave. (b) Colloform surface (8316-10); zeolite pseudomorph from Mt. Hamilton Cave. (c) Conchoidal fracture surface (8516-3); coralloid from Mt. Hamilton Cave.

of any Christiansen effect (see Price and Tetlow, 1948) in the spectra (Fig. 2) shows that the grain size of the samples was sufficiently small for high-quality spectra to be obtained. Since the specimens did not contain Cl, anion exchange with the KBr of the disc could not occur. To ensure maximum consistency between the spectra, all samples were run in the one batch, immediately after weighing.

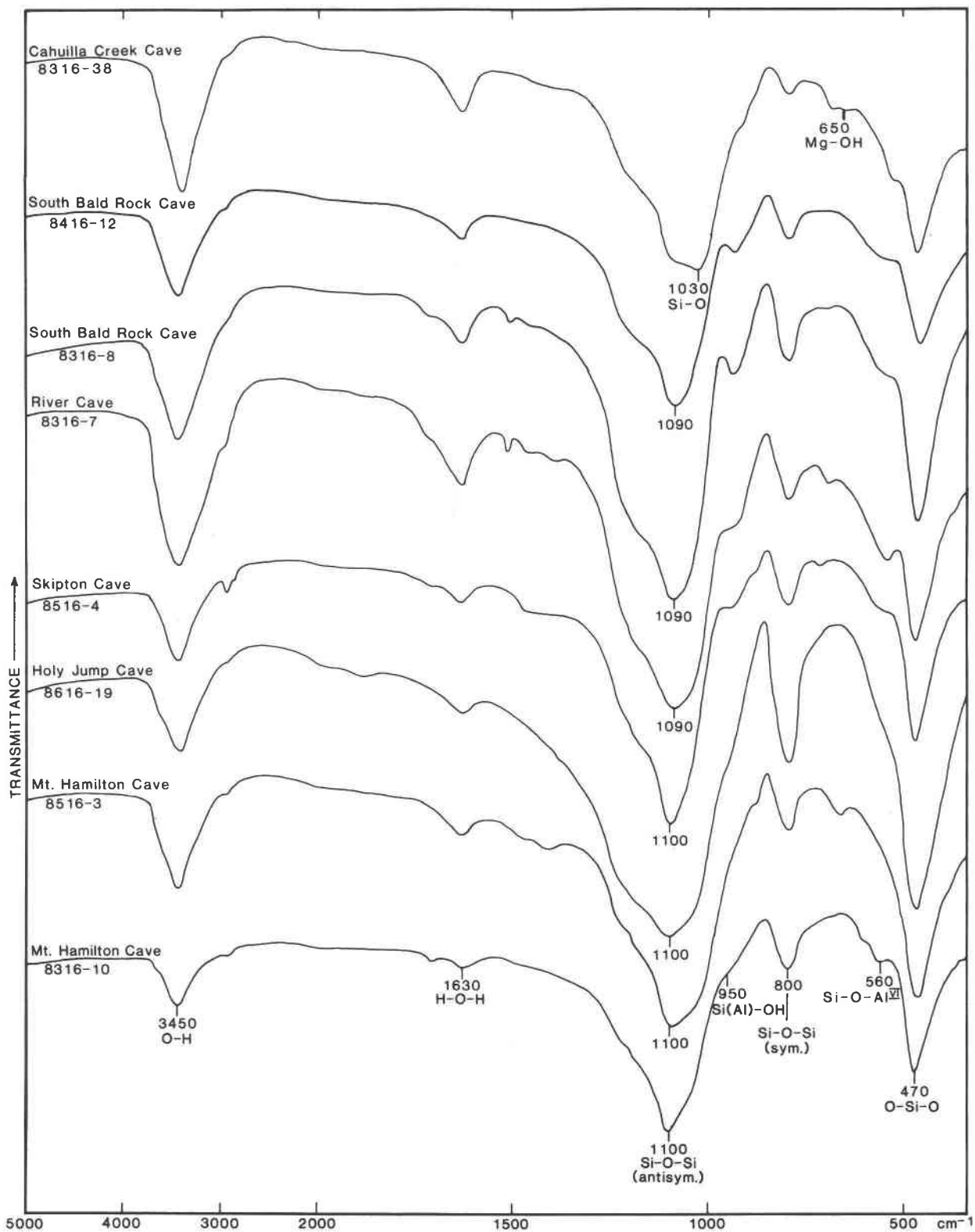


Fig. 2. Infrared spectra of speleothem samples. Cahuilla Creek specimen is poorly crystallized sepiolite; all others are opal-A. Assignments of absorption peaks to bond vibrations applicable to all spectra.

TABLE 1. Chemical analyses of speleothems (in wt%)

Cave	Sample no. and type	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Loss on		Si/(Si + Al) (molar)	
												ignition	Total		
Cahuilla Creek*	8316-38; coralloid interlayers	62.18	0.07	0.32	0.04	0.05	24.62	1.80	0.02	0.02	0.00	n.d.	89.12		
South Bald Rock	8416-12; coralloid	80.71	0.05	5.96	0.37	0.00	0.17	0.09	0.19	0.26	0.40	10.93	99.13	0.93**	
South Bald Rock	8316-8; coralloid	81.44	0.04	5.55	0.40	0.00	0.10	0.12	0.16	0.28	0.67	10.64	99.47		
South Bald Rock*	8316-8; coralloid	86.64	0.00	4.41	0.02	0.00	0.03	0.13	0.09	0.50	0.12	n.d.	91.94	0.94	
River	8316-7; coralloid	69.70	0.08	9.70	2.54	0.01	0.04	0.07	0.23	0.27	1.66	15.61	99.91		
River*	8316-7; coralloid	82.42	0.02	8.41	0.06	0.06	0.04	0.06	0.01	0.05	1.21	n.d.	92.34	0.93**	
Skipton	8516-4; coralloid	89.74	0.11	2.30	0.65	0.00	0.10	0.21	0.25	0.10	0.21	6.18	99.85	0.97†	
Holy Jump Lava	8616-19; botryoidal crust	93.08	0.01	1.02	0.53	0.00	0.28	0.06	0.16	0.06	0.11	3.78	99.09	0.99	
Mt. Hamilton	8516-3; coralloid	81.79	0.05	0.64	0.35	0.00	4.71	3.29	0.13	0.07	0.30	8.02	99.35	0.99	
Mt. Hamilton*	8316-10; zeolite pseudomorph	92.51	0.09	0.00	0.00	0.05	0.07	0.04	0.01	0.02	0.00	n.d.	92.79	1.00	

* Indicates electron-microprobe analyses; all other analyses are XRF (n.d., not determined). Detection limit on XRF analyses is 0.01% or better; on microprobe analyses, it is 0.04% or better.

** Si/(Si + Al) molar ratio adjusted using additional EDS and NMR data; see discussion in text.

† Minimum value because of clay contamination.

The spectra provide interesting data on the short-range (nearest neighbor) structure in the opal and show some differences from the opal spectra obtained by previous workers, e.g., Moenke (1974), Wells et al. (1977), Wilding et al. (1977), Plyusnina (1979). These differences are related to the minor-element composition of the opal, as discussed below.

Al IN OPAL

Previous studies have reported Al₂O₃ levels of up to 4.7% in soil opal (Wilding et al., 1977). Curtiss et al. (1985) and Segnit and Jones (pers. comm.) recorded opals with 17 to 22% Al₂O₃, but these contained large amounts of admixed surface soil and clay.

In the present study, the highest Al₂O₃ levels were found in samples from the Queensland granite caves, ranging from 4.4 to 9.7% Al₂O₃ (Table 1). Part of this Al₂O₃ is due to inclusions of feldspar and allophane (an amorphous hydrous aluminosilicate clay mineral). Very little feldspar is present in these specimens, as shown by thin-section examination and the very low Na, Ca, and K levels in the analyses. On the other hand, allophane is common as very fine grained inclusions concentrated in dark, cloudy growth bands separated by relatively clear interlayers.

In an effort to obtain opal analyses relatively free from allophane contamination, the transparent layers in two specimens were analyzed by electron microprobe (Table 1). The analysis of the South Bald Rock Cave sample (8316-8) appears to represent "pure" opal, but allophane is present in the River Cave analysis, as shown by the relatively high phosphate content (allophane from these caves is phosphate rich; Webb and Finlayson, 1984). In an effort to obtain a better result, a number of clear interlayers in the latter sample were analyzed by quantitative energy-dispersive spectrometry (EDS). The maximum SiO₂/Al₂O₃ weight percentage ratio obtained was 16.4, which converts to a molar Si/(Si + Al) ratio of 0.93 (using the SiO₂ content obtained in the microprobe analysis). This ratio is comparable to that obtained for the allophane-free layers in the South Bald Rock Cave sample

(0.94; Table 1). These results show that the allophane content of the whole speleothems varies from about 1% (South Bald Rock Cave) to approximately 5% (River Cave).

In order to check the amount of allophane in the speleothems, two samples were analyzed by ²⁷Al NMR. This technique determines the relative proportion of tetrahedrally coordinated and octahedrally coordinated Al in a specimen. Allophane contains both types of Al in varying proportions (Farmer, 1985, pers. comm.); if the proportion is known, then the amount of allophane in a sample can be calculated from the ²⁷Al NMR results.

Analysis of one of the opal samples from Mt. Hamilton Cave (8516-3) showed that it contained only tetrahedrally coordinated Al and lacked allophane completely. However, one of the opal coralloids from South Bald Rock Cave (8416-12) has 11% of its total Al octahedrally coordinated. NMR analyses of allophane deposits in the same cave show that about 70% of their Al is octahedrally coordinated. Assuming that the allophane in the opal contains octahedrally coordinated Al in the same proportion, this means that of the 6% Al₂O₃ in the opal (Table 1), approximately 1% is present as allophane (comparable with the other South Bald Rock sample). The remaining 5% occurs as tetrahedrally coordinated Al within the opal, giving a molar Si/(Si + Al) ratio of 0.93. This result compares closely with the ratios obtained above for allophane-free opal from the same area.

Confirmation of these results comes from the IR spectra of the speleothems (Fig. 2). At about 550–560 cm⁻¹ there is a small peak or weak shoulder on most spectra, which represents the vibration of octahedrally coordinated Al in the gibbsite sheets of clays, e.g., kaolinite or allophane (Stubican and Roy, 1961; Farmer et al., 1979). Thus the presence of this peak in the opal spectra indicates clearly that an occluded clay phase is present in many samples. The River Cave opal, with the highest allophane content (~5%), has the most prominent 560-cm⁻¹ peak (Fig. 2). The South Bald Rock samples contain less allophane (~1%) and have smaller 560-cm⁻¹ peaks. The Mt. Hamilton coralloids (8516-3), which according to the ²⁷Al NMR

results lack clay inclusions altogether, have no 560-cm^{-1} peak. The presence of a 560-cm^{-1} peak in the Skipton Cave spectrum indicates clearly that this sample has a small but significant clay content.

One of the Mt. Hamilton samples (8316-10) does not appear to fit this pattern; the IR spectrum has a marked 560-cm^{-1} peak, yet the analysis shows that Al, and hence occluded clay, is absent. However, in this case the samples were collected from fallen material on the floor of the cave and were as a result partially coated with clay, which proved impossible to remove completely. Thus the sample crushed for IR analysis contained a small amount of clay, and this can be seen on the IR spectrum. The chemical analysis was obtained using an electron microprobe; care was taken to keep the beam well away from the clearly visible clay coating, so the analysis shows no evidence of clay.

The IR spectra in Figure 2 also confirm the presence of tetrahedrally coordinated Al substituting for Si in the opal samples. The very strong peak at $1090\text{--}1100\text{ cm}^{-1}$ is due to antisymmetric Si–O–Si stretching vibrations (Moenke, 1974). In tectosilicates the wave number of this peak decreases regularly with increasing substitution of tetrahedral Al into the framework of the mineral (Milkey, 1960), and this effect can be seen in Figure 2. The Queensland granite cave samples have the highest Al_2O_3 contents of the speleothems (molar Si/(Si + Al) ratios of 0.93 to 0.94), and their peaks are at about 1090 cm^{-1} . The basalt cave speleothems have Si/(Si + Al) ratios of 0.97 or greater, and their peaks are at around 1100 cm^{-1} .

Thus this study has shown unequivocally that the Al content of opal is due to occlusion of clay particles as well as substitution of Al for Si. Many authors have proposed or assumed that Al can substitute for Si in the silica minerals (e.g., Dennen, 1966; Frondel, 1962; Flörke et al., 1982), as both elements can occur in tetrahedral coordination and they have similar ionic radii, but direct confirmatory evidence has been lacking.

Replacement of Si^{4+} by Al^{3+} results in a charge imbalance that must be compensated by the entry of monovalent or divalent interstitial ions (e.g., Li, Na, K, Mg, Ca) or by the substitution of a hydroxyl ion for an oxygen to form silanol (SiOH) groups (Dennen, 1966; Wilding et al., 1977; Flörke et al., 1982). The speleothem samples with high Si/(Si + Al) ratios (0.97 or greater) appear to contain sufficient interstitial ions to match, or almost match, the charge imbalance resulting from the Al substitution (exact calculations are impossible because of the presence in some samples of very small amounts of occluded feldspar). Similar results have been reported for microcrystalline quartz of volcanic origin (Flörke et al., 1982). Analyses of the latter samples showed a direct correlation between the content of interstitial ions (Ca + Mg + K + Na + Li) and that of substituted ions (Al + Fe), implying that few, if any silanol groups were incorporated into the quartz structure to balance the charges.

However, this conclusion is definitely not applicable to some of the opal speleothems under study. The high-Al

speleothems from the Queensland granite cases have low levels of interstitial ions and must contain silanol groups to balance the charges. There is evidence for this in the IR spectra (Fig. 2). The 950-cm^{-1} peak in the opal IR spectrum has been ascribed to the Si–O stretching of silanol groups (Moenke, 1974). In the present case it probably also contains a contribution from AlOH groups; micas and clays have well-defined AlOH peaks in this region, due to the in-plane rocking vibration (libration) of hydroxyls linked to two Al ions (Stubican and Roy, 1961; Russell et al., 1970). Thus all speleothem spectra with a 560-cm^{-1} peak due to clay inclusions also have a small 950-cm^{-1} peak or shoulder. However, in the high-Al samples, particularly those from South Bald Rock Cave, the 950-cm^{-1} peak is much larger than the 560-cm^{-1} shoulder. This must be due to the contribution of silanol groups within the opal structure, acting as charge balances for the substituted Al. The speleothems with very weak 950-cm^{-1} shoulders, e.g., Holy Jump Lava Cave, have few silanol groups; apparently the small amount of substituted Al present is balanced by interstitial monovalent and divalent ions.

Mg IN OPAL

Most previously described opals have MgO contents of less than 2% (Wilding et al., 1977). However, the opal variety menilite, which occurs as nodules in limestones and dolomites, typically contains 7 to 8% MgO (Damour, 1884), and Cody (1980) recorded an opal speleothem from a New Zealand lava cave with 14% MgO. Unfortunately, there are no IR data for any of these high-Mg opals, so it is impossible to compare them in detail with the present specimens.

The highest MgO content of the opal speleothems analyzed in this study is 4.7% (Mt. Hamilton coralloids, 8516-3; Table 1). Examination of thin sections of these speleothems using EDS identified calcite inclusions, hence explaining the CaO content of the sample, and confirmed that the Mg is uniformly distributed through the opal.

The Mg is more likely to be interstitial than substituting for silica, as Mg has a larger ionic radius and a lower charge than Si or Al. Spaces in the poorly ordered opal structure can easily accommodate ions of this size, as the well-ordered structures of α -quartz, α -cristobalite, and α -tridymite all contain gaps large enough to allow Mg to enter (Eitel, 1964).

If the interstitial Mg is more abundant than the ions substituting for Si, then there will be a charge imbalance, which must be countered by the introduction of OH groups chemically bonded to the interstitial ion rather than the Si of the opal. The IR spectrum of the Mt. Hamilton coralloids (8516-3, Fig. 2) provides strong evidence that this is indeed the case. The spectrum has a small but definite peak at about 660-cm^{-1} , which is not present in any of the other opal spectra. The hydrous magnesium silicate talc possesses a prominent IR peak at approximately 670 cm^{-1} , representing the in-plane vibrations of hydroxyls coordinated to three Mg atoms (Russell et al.,

1970). The IR spectrum of sepiolite, a hydrous magnesium silicate clay mineral, has a peak in a comparable position (650 cm^{-1} ; Nagata et al., 1974), apparently due to a similar Mg-OH vibration. Thus the presence of this peak in the Mt. Hamilton spectrum indicates clearly that the Mg in the sample is directly bonded to hydroxyls.

The Cahuilla Creek sample is a poorly crystallized sepiolite. It has a molar Mg/Si ratio of 0.59, close to that of sepiolite (0.61–0.67; Wollast et al., 1968), but its birefringence is much lower than that of sepiolite, and it lacks well-defined XRD peaks. Nevertheless, the IR spectrum (Fig. 2) is very similar to that of sepiolite, particularly in the $450\text{--}900\text{-cm}^{-1}$ region. The major Si-O peak in the sepiolite spectrum is at 1020 cm^{-1} , with a smaller peak at about 1070 cm^{-1} ; the shapes and positions of these peaks can vary slightly (compare Wollast et al., 1968; Nagata et al., 1974; Yenyol, 1986), probably due to differences in composition. The very broad profile of these two peaks in the Cahuilla Creek spectrum is similar to that figured by Wollast et al. (1968), although the Cahuilla Creek peaks are at slightly higher wave numbers (1030 and 1090 cm^{-1}).

Comparison of the Cahuilla Creek and Mt. Hamilton (8516-3) IR spectra in the $1000\text{--}1100\text{-cm}^{-1}$ region raises an interesting point. There is a marked shoulder on the Mt. Hamilton spectrum at about 1030 cm^{-1} . By analogy with the Cahuilla Creek spectrum, this could be due to Si-O vibrations of a magnesium silicate phase within the opal; the Si-O vibrations of the opal itself are represented by the very strong 1100-cm^{-1} peak. If this assignment of peaks is correct, it indicates that the Mg in the opal is present not as individual interstitial ions, but as hydrous magnesium silicate domains of sufficient size and abundance to be evident on the IR spectrum. EDS scanning of thin sections of the Mt. Hamilton coralloids showed that the Mg distribution in the opal is quite uniform, so if the above hypothesis is correct, then the magnesium silicate domains must be relatively small and randomly distributed.

The incorporation of interstitial Mg within the opal-A structure is not unexpected, as $\text{Mg}(\text{OH})_2$ displays a strong affinity for silica and can flocculate undersaturated silica solutions (Williams and Crerar, 1985). Because $\text{Mg}(\text{OH})_2$ carries a positive surface charge under most natural conditions, it can neutralize the negative surface charge of silica particles in solution and allow them to precipitate. The neutralizing cations are readily incorporated into the growing surface of the silica precipitate.

WATER IN OPAL

Previous studies have shown that opal usually contains between 3% and 11% water (Segnit et al., 1965; Wilding et al., 1977). Allophane-free opal in the speleothem samples contains up to 8% water (microprobe analyses in Table 1). The loss on ignition for the granite-cave specimens is greater than this (up to 15%) because of the occluded allophane, which contains about 40% water and organic compounds (Webb and Finlayson, 1984).

Water in opal occurs as molecular water, silanol (SiOH) groups, and hydroxyls bound to interstitial ions. The molecular water is present as capillary condensation in pores within the opal (Segnit et al., 1965) and as isolated molecules trapped in small interstices within the silica matrix (Langer and Flörke, 1974). The silanol groups exist both as a monolayer of hydroxyl groups attached to the surface Si atoms (i.e., a surface silanol layer; Iler, 1955) and as isolated SiOH groups within the SiO_2 framework, compensating for the charge imbalance caused by ions substituting for Si, as discussed previously. The present study has also shown that water in opal may be present as OH groups bound to interstitial ions, particularly Mg, when these ions are more abundant in the opal than ions substituting for Si.

Thus the minor-element content of an opal is of prime importance in determining the proportion of OH groups in the opal, bound to both Si and interstitial ions. For example, the high- Al_2O_3 samples from South Bald Rock have abundant silanol groups (as shown by the strong 950-cm^{-1} IR peaks on Fig. 2), in this case formed to charge-balance the substituted Al. On the other hand, the Mt. Hamilton coralloids (8516-3) have very few silanol groups (no significant 950-cm^{-1} peak), but the 660-cm^{-1} MgOH peak shows clearly that hydroxyl groups are present in the structure, in this case bonded to the interstitial Mg.

The 1630-cm^{-1} IR peak results from the H-O-H bending vibrations of molecular water (Langer and Flörke 1974), so the strength of this peak reflects to some extent the content of molecular water in the sample. All the speleothems have definite 1630-cm^{-1} peaks (Fig. 2) and so contain molecular water. The River Cave speleothem has the largest peak, probably due to the contribution from molecular water in the allophane inclusions.

Langer and Flörke (1974) used near-infrared spectra to estimate the relative proportions of molecular and silanol water in opal samples. They found that, in general, hyalites had the highest percentage of silanol groups (up to 40% of total water), whereas opal-AG specimens had only 10 to 15% of their water as silanol groups. Langer and Flörke (1974) did not consider the minor-element content of the opals when attempting to explain this difference. Instead they suggested that the temperature of the depositing solution might have been a significant cause. Numerous OH groups could be more easily incorporated into the hyalite structure because it is deposited by quenching from high-temperature solutions.

However, in the present study, the single hyalite sample (Holy Jump) has very few silanol groups (as shown by the very weak 950-cm^{-1} peak), and, in fact, one of Langer and Flörke's hyalite specimens also contained a low proportion of silanol groups (about 10% of total water). Furthermore, several of the opal-AG speleothems, particularly those from South Bald Rock Cave, have a much greater proportion of silanol groups. The present study has shown that minor elements play a major role in determining the hydroxyl content within the opal structure, and this effect is apparently sufficient to

override any differences due to the temperature of the solutions forming the opal.

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